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PROSPECTS FOR THE RECOVERY OF GOLD FROM CYANIDE LIQUORS AND PULPS BY SOLVENT EXTRACTION AND BY ION EXCHANGE

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June 1988

Project: 30.61.02
Gold

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 88-78 (IR)

108 pp

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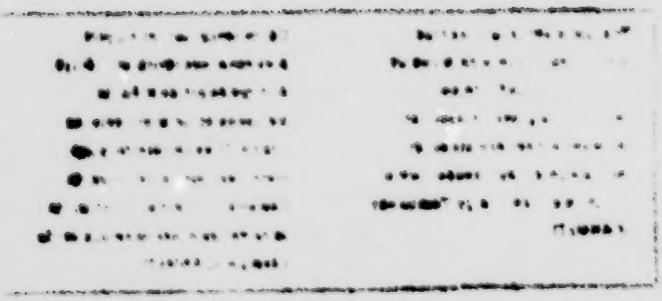

Prospects for the Recovery of Gold from Cyanide Liquors and Pulps by Solvent Extraction and by Ion Exchange

by David M. Muir[+]

Abstract

A review of current developments in resin and solvent technology as possible alternatives to carbon for recovering gold from cyanide leach slurries has been carried out together with an analysis of the costs associated with gold mining and processing to establish the economic constraints for any new process. Recent studies have shown that currently available commercial resins have attractive physical properties but limited chemical properties and do not compare favorably with carbon economically. New solvent extractant systems, however, particularly quaternary amines like Aliquat 336, offer the prospect of better chemical properties provided solvent losses are not excessive. The quaternary amine system coupled with air-sparged thiourea stripping appears to have merits for applications to clarified leach solutions but the best economic advantage is gained if solvents can be applied to pulps directly.

A survey of previous solvent-in-pulp (SIP) work on uranium leach slurries using a tertiary amine extractant like Alamine 336, identified a number of practical problems and variable solvent losses. Thus a detailed investigation of the various factors involved in SIP has been undertaken with particular regard to understanding the principles and causes of emulsion and crud formation, flocculation, and adsorption of organics on mineral surfaces. Tests have been carried out to

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determine the best type of flocculant for SIP on a local ore and to establish adsorption isotherms for Aliquat 336 and Alamine 336 on a silicate ore, pure quartz, a pyrite concentrate and pure pyrite. The effects of particle size, pH and various inorganic and organic pre-treatment additives were examined to try to minimise amine adsorption. It was found that adsorption of amine onto the pulp also led to adsorption of $Au(CN)_2^-$ from the liquor resulting in poor gold recovery. Rates of transfer of Aliquat 336 and $Au(CN)_2^-$ between water and the organic phase were found to be comparable and apparently limited by mass transfer across the interface. Moreover, using contactor designs with minimum agitation to prevent dispersion of the organic, rates of $Au(CN)_2^-$ extraction were very slow. More consideration of the organic adsorption onto minerals and contactor design is needed before SIP can offer a viable alternative to CIP.

Keywords: gold, solvent extraction, amines, surface chemistry, solvent-in-pulp, ion exchange, resin, resin-in-pulp

Perspectives de récupération de l'or contenu dans des liqueurs et des boues de cyanuration par extraction au solvent et échange d'ions

par David M. Muir*

RESUME

Un examen des progrès récents en matière de technologie des résines et des solvants comme produits éventuels de remplacement du carbone pour la récupération de l'or dans les boues de lixiviation au cyanure, ainsi qu'une analyse des coûts associés à l'exploitation et au traitement de la roche aurifère visant à établir les contraintes économiques de tout nouveau procédé, ont été réalisés. Des études récentes ont montré que les résines actuellement disponibles dans les commerce ont des propriétés physiques intéressantes, mais des propriétés chimiques limitées, et ne se comparent pas favorablement au carbone sur le plan économique. De nouveaux solvants d'extraction, notamment les amines quaternaire comme l'Aliquat 336, semblent avoir de meilleures propriétés chimiques dans la mesure où les pertes de solvant ne sont pas excessives. Le traitement aux amines quaternaires, couplé à l'extraction par la thiourée en aérosol, semble avoir des applications prometteuses pour le traitement des solutions de lixiviation clarifiées, mais le plus grand gain économique proviendra du traitement direct des boues par des solvents.

Une étude de travaux antérieurs sur le traitement des boues, notamment des boues de lixiviation de l'uranium, par des solvants, notamment des agents d'extraction à base d'amines tertiaires comme l'Alamine 336, a montré que des problèmes pratiques se posaient et que les pertes de solvant étaient variables. Un examen détaillé des divers facteurs intervenant dans le traitement des boues par solvants a été entrepris, portant en particulier sur la compréhension des principes et des causes d'émulsion et de formation de dépôts non désirables, de floculation et d'adsorption de matières organiques sur la surface des minéraux. Des essais ont été menés pour déterminer le meilleur type de floculant à utiliser pour le traitement des boues d'un minerai local par des solvants et pour établir des isothermes d'adsorption de l'Aliquat 336 et de l'Alamine 336 sur un minerai de silicate, du quartz pur, un concentré de pyrite et de la pyrite pure. Les effets de la taille des particules, du pH et de divers additifs de prétraitement tant inorganiques qu'organiques ont été examinés pour tenter de minimiser l'adsorption des amines. Il a été établi que l'adsorption d'un amine sur la boue se traduisait par l'adsorption d'$Au(CN)_2^-$ provenant de la liqueur, donc par une faible récupération de l'or. Les vitesses de transfert de l'Aliquat 336 et de l'$Au(CN)_2^-$ entre l'eau et la phase organique se sont avérées comparables et apparemment limitées par le transfert de masse à travaers l'interface. En outre, même en utilisant des modèles de contacteurs minimisant l'agitation pour empêcher la dispersion de la matière organique, on a obtenu des taux d'extraction d'$Au(CN)_2^-$ très faibles. Il faudra étudier davantage l'adsorption des matières organiques sur les minéraux et améliorer la conception des contacteurs avant que le traitement des boues par solvants ne puisse remplacer avantageusement leur traitement au carbone.

Mots clés: or, extraction au solvant, amines, cimie des surfaces, traitement des boues par solvants, échange d'ions, résine, traitement des boues par résines

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PROSPECTS FOR THE RECOVERY OF GOLD FROM CYANIDE LIQUORS AND PULPS BY SOLVENT EXTRACTION AND ION EXCHANGE

I. REVIEW OF CURRENT TECHNOLOGY

Introduction

Although the carbon-in-pulp (CIP) process is well established and economically viable for recovering gold from cyanide leach slurries, alternative technologies utilising resins or solvent extractants have attracted considerable interest to try to overcome some of the inherent problems with carbon. Such problems include [1,2]:

i) the relatively low loading of gold on carbon;
ii) the physical fouling of carbon by $CaCO_3$, Fe_2O_3, SiO_2(clays), $Cu(OH)_2CuCO_3$, etc., which blocks pores;
iii) the chemical fouling by process organics like xanthates, frothers, humates, kerosene and lubricants which deactivate the surface;
iv) the attrition of carbon in the pulp and in screening/handling;
v) the need to reactivate carbon by kilning, and attendant losses of carbon;
vi) the difficulty in stripping $Au(CN)_2^-$ from carbon;
vii) the dependence on overseas supply of coconut shell carbon.

The main advantage of carbon lies in its ability to be used directly in the pulp, thereby eliminating the need for expensive thickeners and clarifiers and avoiding losses of $Au(CN)_2^-$ in the wet filter cake. Thus any new technology should also be applicable to pulps to have a real economic advantage, as well as provide a simpler or more efficient method of recovering gold. Resin-in-pulp techniques have been successfully developed for the

uranium industry in the 1970s [3] and continuous fluidised-bed ion-exchange columns can provide the automation necessary to simplify the resin loading or stripping operations. The loading, screening and transfer of resin from gold-cyanide liquors has also been successfully demonstrated on a pilot scale in South Africa [4,5]. Unfortunately, as discussed below, no resin has yet been developed which can offer the selectivity and loading characteristics required to process dilute $Au(CN)_2^-$ leach solutions contaminated with other cyano-complexes like $Cu(CN)_2^-$, $Fe(CN)_6^{4-}$, $Ni(CN)_4^{2-}$ and $Zn(CN)_4^{2-}$ as well as CN^-, Cl^- and SO_4^{2-} all at much higher concentrations than gold [6].

Solvent extractants on the other hand have been developed which offer higher loadings and better selectivity than resins. Solvents also have the advantage of offering faster kinetics of extraction, and avoid the problems of fouling by Co, Fe or silica, and osmotic shock upon stripping which plague many resin systems. Their applicability to pulps or even clarified leach liquors is still in question. Testwork on solvent-in-pulp techniques for uranium leach pulps in the 1960's and 1970's identified problems with the formation of emulsions or excessive crud and sometimes excessive solvent losses[7]. However, Ritcey et al reported that emulsions could be avoided using sieve-plate columns rather than conventional mixer-settlers and found that solvent losses and crud formation were reasonably low when treating certain uranium-bearing dilute sulfuric acid pulps with tertiary amine extractants [8]. Pilot tests with various ores unfortunately gave erratic results and no systematic or fundamental study of solvent losses and solvent-mineral interactions has been carried out.

The relative advantages of solvent extractants over resins for gold recovery has recently revived interest in reinvestigating and developing the solvent-in-pulp technology further [9]. The aim of this report is firstly to review the current progress in new resins and solvents, and to consider the practical and economic constraints for solvent-in-pulp; secondly

to investigate the causes and mechanism of solvent and gold losses and to consider possible means of minimising such losses. It should be recognised that the processing of very dilute gold cyanide pulps represents the most difficult situation. Even if unsuccessful in this context, a better understanding of the SIP process may lead to successful development for other extractant or pulp systems or lead to the successful treatment of clarified leach liquors with solvents. With the increasing popularity of heap leaching of low grade gold ores, particularly in the U.S.A. [10,11], there is scope for the development of solvents to treat these relatively clean clarified liquors provided they can match or exceed the loading and selectivity characteristics of carbon without excessive soluble losses in the raffinate.

Economic Constraints for New Technology

The high value of gold compared with other metals often distorts sensible economic judgement when considering new technology. Expensive equipment, chemicals or processing schemes may be thought to be viable because they represent only a small fraction of the market price of gold. In fact, whilst some gold mines are highly profitable, many are marginally economic and each stage of the processing operation must be scrutinised to identify cost savings. The problem with gold mining compared with other metals is that the grade and complexity of the ore can vary enormously as well as the size of the operation and ore reserves.

Company reports in 1987 indicated that the operating costs to produce 1 oz Au ranged from CDN $126-465, (Table 1). This cost excludes capital depreciation (estimated to be ≈$100/oz Au) profits, taxes, etc.

Table 1 - 1987 Operating Costs to Produce 1 oz Au by Various Mines (Ref. Report on Business July 1988)

Giant Yellowknife Mines	CDN $465
LAC Minerals	CDN $314
Hemlo Gold Mines	CDN $126
Dome Mines	CDN $309
American Barrick	CDN $278
Echo Bay Mine	CDN $268
Average of 20 companies	CDN $310

Table 2 - Average Cost of Seven U.S. Gold Producers (1984 US$) [12]

Costing Area	Heap Leaching	CCD/CIP or CIL
	$	$
Capital ($1000/ton)	5,260[a]	15,610[a]
	(Range 3-8,000)	(Range 8-24,000)
Operating ($/ton)	4.80[b]	10.20[b]
	(Range 3-7)	(Range 5-16)
Major Reagents ($/ton)	0.70[c]	3.10[c]
Open-Pit Mining	1.05[b]	1.05[b]

a) includes infrastructure, ancillaries, tailings disposal, site costs, etc.
b) includes all site and administration costs, but excludes depreciation, taxes, capital replacement and debt servicing
c) deposit specific reagents excluded

In a survey of capital and operating costs of seven Western U.S. gold and silver producers in 1984, ranging in size from <1000 tonnes per day to 5000 tpd, Griffiths [12] found that capital and operating costs varied by up to a factor of three

because of the variation in size and grade. Heap leaching proved to cost less than half the cost of CIP or CIL but, of course, this was offset by lower grades and recoveries (Table 2).

Based on these average costings, a breakdown of costs in terms of $/oz Au produced, can be readily calculated for a 3000 tpd operation using either CIP for an ore grade of 2.8 gt^{-1} recoverable Au, or heap leach for an ore grade of 0.7 gt^{-1} recoverable Au, as shown in Table 3.

Table 3 - Cost Analysis for 3000 tpd Mining Operation
(330 days/annum)

	1984 US$/oz Au Recovered	
	Heap Leach (0.7 gt^{-1} Au)	CIP (2.8 gt^{-1} Au)
	$	$
Capital Repayment @ 20%/annum	125	93
Mining Costs	84[a]	42[b]
Operating Costs	192	102
Reagent Costs	28	31
	$429	$268

a) overburden: ore ratio of 2:1, b) overburden: ore ratio of 4:1

This table demonstrates the marginal profitability of a low grade heap leaching operation compared with the modest profitability of CIP, using average ore grades. Significantly, the overall cost of chemicals and reagents is only about 10% of the value of gold produced.

More detailed operating cost analyses for a 3000 tpd operation have been presented by McQuinston and Shoemaker [13] on the Battle Mountain Mine (Nevada) and, more recently, by Wicks on the Barrick Mercur Mine (Utah) [14]. The Mercur Mine operates both a heap leach as well as a CIP operation, and has recently turned to pretreating refractory carbonaceous ores by pressure

leaching at 220°C and 475 psi O_2. Estimated running costs in 1986 for each of these operations are summarised in Table 4.

Table 4 - Operating Costs for Heap Leach, CIP, and Refractory Ore Pretreatment at Mercur Mines (Utah) in 1986 for 3000 tpd Operation [14]

	US$/oz Au Recovered
Mining Costs (3.5:1 overburden)	52
Milling Costs[a]	132
Heap Leach[b]	119
Refractory Ore Pretreatment[c]	127

a) Processing high grade (>2.5 gt^{-1} Au) and low grade (1-2.5 gt^{-1} Au) ore. Assuming average = 1.4 gt^{-1} recoverable Au. b) For 0.7-1.0 gt^{-1} Au ore.
c) For 2 gt^{-1} Au, 1.7%S ore. Reagents = $77/oz Au, labour = $31/oz Au, power = $11/oz Au.

A complete breakdown of mill costs of the two mining operations is presented in Table 5. Because the two operations were costed in 1986 and 1980, an inflation factor of 100% has been assumed to apply to the Battle Mountain operation. This places mill costs at Battle Mountain in the higher range compared to other mines (Tables 2 and 3) mainly as a result of the high cost of leaching and tailings disposal.

Table 5 - Mill Costs for Mercur Mine (Utah) and Battle Mountain (Nevada) - in U.S.$

	Mercur Mine (1986)		Battle Mtn. (1980)	
Capacity	tpa	3000	2720	
Grade	gt^{-1}	1.4	2.7	
Mill costs $/ton ore				
Crushing/screening/handling	1.02	52	1.49	31[c]
Grinding/classifying	1.59		2.01	42[c]
Leaching	1.55	31	3.37	71[c]
Carbon stripping[a]	0.37[a]	7.4	0.61[b]	13[c]
Electrolysis/refining			0.39	
Carbon regeneration	0.17	3.4	-b	
Tailings disposal	0.16	3.3	1.97	42[c]
Assaying/overheads	0.51	10.2	1.13	24[c]
General	-		0.52	
Administration	1.14	22.8	1.72	36[c]
Overall	$6.51 /ton ore	$132 /oz Au	$13.21 /ton ore	$278[c] /oz Au

a) using Zadra elution; b) using ethanol/Zadra and includes carbon regeneration cost; c) assuming double costs due to inflation 1980-86.

The significant feature of those cost analyses is the relatively low cost of carbon stripping, electrowinning and regeneration compared to classification leaching and general management or servicing. Stripping operation costs for chemicals and energy have been estimated separately [15] to be about $300-450/tonne carbon loaded to 4000 gt^{-1} Au, i.e., $3/oz Au, whilst basic carbon regeneration costs have been estimated at $400/tonne ($3/oz Au) based upon power consumption of 1.6 kWh/kg C and carbon losses of 5%. A realistic breakdown of costs for gold producers in 1986 therefore appears to be in the ranges

summarised by Table 6, with the average cost for all reagents (carbon, NaCN, NaOH, HCl, etc.) about $35/oz Au produced.

Table 6 - Summary of Gold Production Costs

	1986 US $/oz Au produced
Mining	50 - 80
Milling (crush, grind, classify)	35 - 70
CIL/CIP	20 - 70
Carbon stripping, E/win and regeneration	8 - 21
Admin., assays, tailings, etc.	30 - 100
Capital costs, interest, etc.	60 - 150

It is clear from this analysis that with regard to just processing, new technology will only be accepted if it can be demonstrated to improve the recovery or efficiency of gold recovery, or to simplify the operation (leading to lower capital or operating costs), or to speed-up the processing (leading to higher throughput or lower gold inventories in circuit) or to overcome problems associated with conventional practice. High costs of chemical reagents or equipment must be offset by economies in other areas. The best opportunity for new technology exists when conventional practice cannot deal with the situation, just as CIP started as a process to treat slimy ores. Thus resin or solvent technology is more likely to gain acceptance for treating ores which carbon cannot process, e.g., ores contaminated with organic foulants. If resins or solvents are to compete economically with carbon, the losses of resin or solvent, and all other chemicals required should amount to no more than $25/oz Au produced, assuming all other unit operations remain the same.

Developments with Resins

a) Loading and Selectivity

Testwork with commercial weak-base (tertiary amine) and strong-base (quaternary ammonium) resins has been reviewed by Hosking [16] and by Riveros and Cooper [17]. Comparative data on the performance of various strong-base resins and coconut shell carbons in actual plant liquors have been recently reported by Fleming and Cromberge [18], and Riveros [19], whilst the comparative performance of a number of commercial weak-base resins has been reported by Palmer [20]. Table 7 illustrates the loadings reported on particular weak- and strong-base resins and activated coconut shell carbon after contact with a range of different feed solutions which vary widely in their concentration of $Au(CN)_2^-$ and relative concentration of other metal cyanide species. Although loadings vary considerably and are influenced by other factors such as pH and free $[CN^-]$, the distribution coefficient of gold and the selectivity of gold over copper, nickel, zinc and iron are useful indicators of resin or carbon performance. These can be derived from the loading data, as also shown in Table 7. In general, these results and others show that:

1) Weak-base resins are more selective for gold than strong-base resins but loadings are much lower.
2) Selectivity decreases with mixed functional group resins, according to the proportion of quaternary ammonium groups to tertiary amine groups.
3) Selectivity decreases as the degree of cross-linking increases.
4) Loading increases as the surface area or porosity of the resin increases.
5) Weak-base resins load poorly at pH 10.
6) High levels of other metal cyanides effectively compete for $Au(CN)_2^-$ onto strong-base resins.

7) Au/Cu selectivity varies with free CN^-, particularly with carbon, due to changes in $Cu(CN)_2^-$:$Cu(CN)_3^{2-}$ ratio.
8) $Zn(CN)_4^{2-}$ and $Co(CN)_6^{3-}$ load strongly onto resins but not onto carbon.
9) Background salts increase the gold loading onto carbon but depress the loading onto weak-base (in particular) and strong-base resins.

The strong adsorption of $Au(CN)_2^-$ onto strong-base resins however presents problems in stripping. Unlike weak-base resins which are readily stripped of gold by raising the pH with NaOH solutions, strong-base resins require special elution procedures and regeneration. Proposed elution procedures involve the use of acidified thiourea or diluted HCl in acetone, SCN^- in aqueous DMF or DMSO, SCN^-/Fe^{3+}, or electro-elution with $Zn(CN)_4^{2-}$ [16,17,21]. None of these procedures are simple or cost-effective compared with the elution of activated carbon, and none effectively removes resin "poisons" such as "Prussian blue", $Co(CN)_6^{3-}$, and silica.

b) Costs

In a recent detailed economic comparison, Lakshmanan et al [22] focussed on evaluating the cost of recovering a gold eluate from a clarified heap leach liquor assaying 3 ppm Au flowing at 4000 litres per minute, using either a continuous fluidised bed strong-base ion exchange system or an activated carbon train. To provide the simplest and most efficient model, it was assumed that the liquor contained no competing cyanide species and that 98% of the gold could be recovered by stripping the resin

Table 7. Loading and Selectivity of Weak-Base and Strong-Base Resins with Metal Cyanides and Comparison with Activated Carbon

	Resin/Carbon/Solution Analysis (ppm)					Au loading	Selectivity Factor[b]			
	Au	Cu	Ni	Zn	Fe	Factor[a]	Au/Cu	Au/Ni	Au/Zn	Au/Fe
1. Weak Base vs Strong Base Resin [16]										
Feed Solution	17.5	4.1	2.2	0.7	2.2					
De-Acidate H (10% SB)	13800	410	600	530	320	788	7.8	2.9	1.0	5.4
De-Acidate H (46% SB)	41500	3100	3800	900	1500	2370	3.2	1.4	1.8	3.5
De-Acidate H (90% SB)	47200	12300	4200	950	9600	2700	0.9	1.4	2.0	0.6
2. Various Strong Base Resins [19]										
Feed Solution	10.0	85	43	34	31					
Amberlite IRA400	1480[c]	5000[c]	11500[c]	15000[c]	3500[c]	148	2.5	0.6	0.3	1.3
Dowex MSA-2	1500[c]	2500[c]	7500[c]	10000[c]	2500[c]	150	5.1	0.8	0.5	1.8
Duolite A101D	1200[c]	4200[c]	10500[c]	13500[c]	3000[c]	120	2.4	0.5	0.3	1.2
Feed Solution	6	4.7	1.5	0.2	14					
Amberlite IRA400	4325[c]	2800[c]	1400[c]	<500[c]	9000[c]	721	1.2	0.8	-	1.1
3. Carbon vs Weak Base Resin [16]										
Feed Solution 1	5.8	2.1	<1	4.9	1.2					
AM-2B (16% SB)	13900	2000	700	19000	2000	2400	2.5	<3	0.6	1.5
Coconut Carbon	9200	100	40	100	1500	1590	33	<40	77	1.3
Feed Solution 2	0.8	3.0	0.5	0.3	7.5					
AM-2B (16% SB)	13500	5000	600	2000	5000	16800	5.0	14	2.5	27
Coconut Carbon	4000	1500	1000	2000		5000	4.4	2.5	1.3	4.3
4. Carbon vs Strong Base Resin [18], [22]										
Feed Solution	2.7	8.5	2.8	1.7	0.25					
SB resin	6.50	15000	7500	5500	1400	2278	1.4	0.8	0.7	0.4
Coconut Carbon	5850	200	3600	<100	300	2166	98	1.6	>40	1.8
Feed Solution	10.0	76	41	32	25					
IRA 400	1384[c]	9792[c]	6350[c]	3046[c]	2278[c]	138	1.1	0.9	1.5	1.5
Coconut Carbon	16930	30000	28425	27912	2750	1693	4.3	2.5	2.0	15.4

a) $[Au]^{solid}:[Au]_{soln}$; b) $[Au:M]^{solid}:[Au:M]_{feed}$; c) as gms per litre of wet resin.

either by electro-elution with $Zn(CN)_4^{2-}$ or with KSCN in aqueous DMF. Resin losses per annum were set at 10% whilst carbon losses were estimated to be 20%.

The results of this evaluation, summarised in Table 8, show that plant capital costs were about 30% less using a single-stage fluidised bed ion exchange column rather than a five-stage carbon adsorption train, but the high initial cost of resin ($\approx$\$10,000 m^{-3}) compared with carbon ($\approx$\$1,500 m^{-3} or \$4,000 t^{-1}) increased the total capital costs of the resin system to 60% greater than the carbon system. Furthermore, the operating costs for the resin system was 10-50% higher than that for the carbon system, depending on the elution method of choice, mainly as a result of the high cost of chemicals and resin makeup.

Table 8 - Estimated Capital and Operating Costs Comparisons for Loading and Eluting Strong-Base Resin and Activated Carbon, Using Clarified Liquors [18]
(Flow = 4000 $lmin^{-1}$ @ 3 ppm Au)

	I Resin	II Resin	III Carbon
Plant cost	\$426,000	\$458,000	\$617,000
Adsorbent cost	689,200	748,200	95,800
Operating cost \$/annum	475,000	380,000	337,000

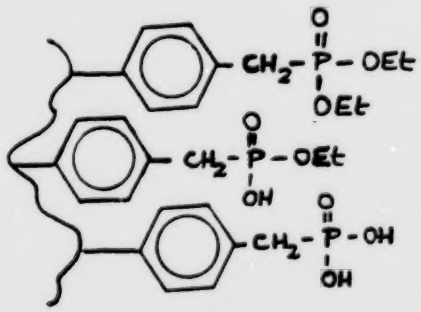
I using $KSCN/H_2O/DMF$ eluant; II using $Zn(CN)_4^{2-}$ eluant; III using NaCN/NaOH atmospheric Zadra procedure.

c) New Developments

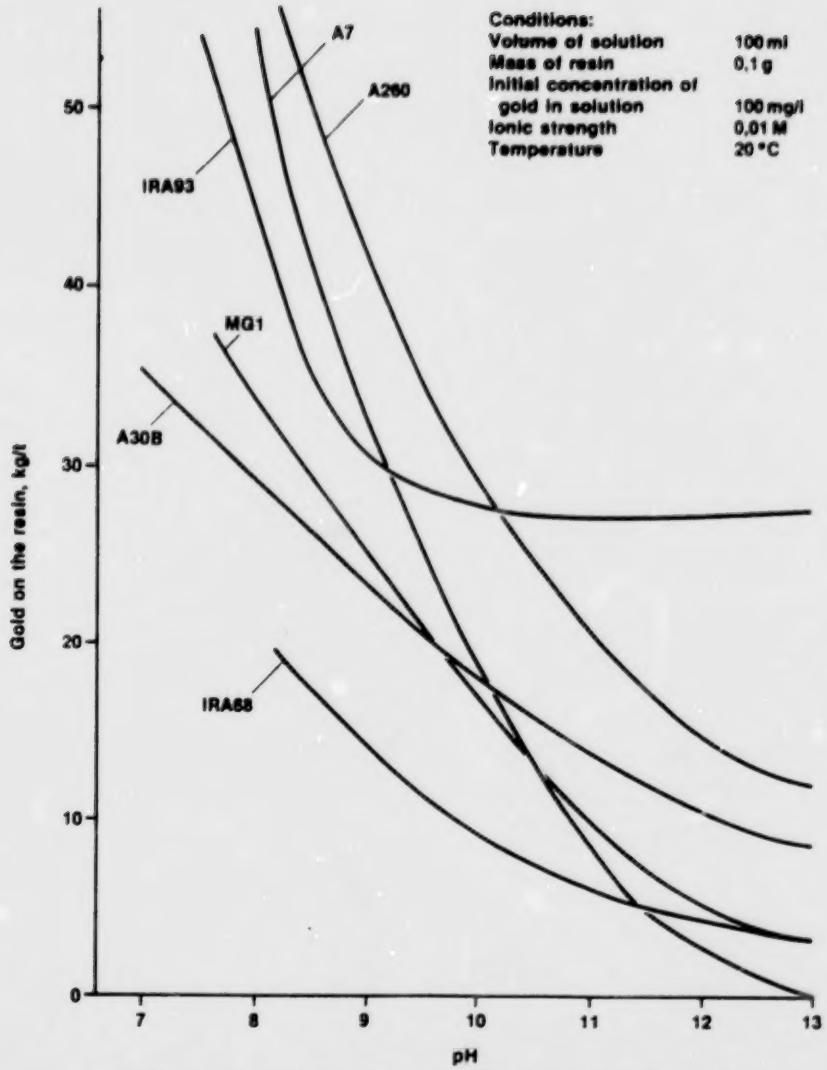
Although weak-base resins may not be much cheaper than strong-base resins, these resins offer much simpler stripping procedures; thus more recent efforts have been directed to developing new or improved weak-base resins. Unfortunately, it is inherently difficult to synthesise simple tertiary amine functional resins without some quaternary ammonium functionality

being present which binds the $Au(CN)_2^-$ strongly. The variable elution performance of several commercial resins shown by Figure 1 [6] and recent testwork by Bartlett on a series of Dow experimental weak-base resins [23] clearly demonstrates this problem. Whilst good selectivity and loading of gold could be obtained with certain macroporous resins with very little attrition in the pulp, at the best, only 62% of the gold could be readily eluted with 1% NaCN/1% NaOH at 90^{o} [23]. Furthermore, different batches of the same resin gave different elution efficiencies. Dow Chemicals Ltd. is reportedly active in synthesising and testing other types of gold selective resins which may lead to a break-through in the next few years.

New weak-base functional groups are also being investigated by MINTEK [24], whilst at the University of Utah, novel phosphonate-ester-acid-based resins have been recently evaluated [25] which involve an ion-pair adsorption mechanism with $NaAu(CN)_2$ similar to activated carbon.



These resins differ fundamentally from conventional weak-base resins in that they are insensitive to pH and load gold more effectively in NaCN/NaOH solution. Stripping is accomplished by raising the temperature and lowering the ionic strength of the solution, as is carried out with carbon. According to the functional group composition, the distribution coefficients measured for gold, copper, and iron after equilibration in 1 ppm metal cyanide solutions, containing 0.1M NaCN/NaOH, are reported to be 1150, 180 and 64, respectively. Current research by Wan et



—Effect of pH on the equilibrium loading of aurocyanide onto weak-base resins (0,1 g of each) from a solution containing potassium aurocyanide alone

Fig. 1 - Stripping characteristics of several commercial weak base resins with NaOH. [Ref. 6]

al is focussing on the performance of novel bifunctional amine/phosphorus resins which exhibit dependence on both pH and ionic strength of the media [26]. Preliminary results suggest, however that like weak-base resins, it is difficult to completely strip the gold and that the selectivity for gold is not high.

Thus, while modest loadings and selectivities are achieved with new resin types, as yet, they do not match the loading of conventional resins, and current resin technology is still not able to offer a viable economic alternate to carbon except for specific problem pulps where carbon is unsuitable as an adsorbent.

Developments with Solvent Extractants

a) Basic Studies

Until recently the main application of solvent extractants for gold has been for analytical purposes, usually as a method of pre-concentrating dilute solutions of $AuCl_4^-$ or $Au(CN)_2^-$ for atomic adsorption analysis or as a means of avoiding interferences from high background salt concentrations in solution. In such applications, loadings, selectivity, solvent losses, and gold recovery from the solvent are of no concern. Solvents such as MIBK, DIBK or Dibutyl carbitol (DBC) are popular to extract gold from chloride media as $H^+AuCl_4^-$ species by a solvating ion-pair mechanism [27]. For $Au(CN)_2^-$ extraction, more quantitative recovery is achieved if 1-2% Aliquat 336 (tri-(C_8-C_{10}) alkyl methyl ammonium chloride) or similar quaternary amines are added to the solvent, which then extracts gold by an anion exchange mechanism.

The development of solvent extraction processes for refining precious metal residues or platinum group metals in the 1970s resulted in greater attention being paid to developing systems in which gold could be extracted and recovered from moderately concentrated leach solutions. Because gold was predominantly extracted as $AuCl_4^-$, it could be readily recovered by stripping using SO_2, oxalic acid, or $FeSO_4$ to precipitate Au powder directly from the organic phase. In this context, DBC is used to extract gold in the Inco Process [28] and MIBK in the Johnson-Matthey Process [29]. More recently Demopoulos et al announced a novel solvent extraction and recovery procedure for $AuCl_4^-$ using Kelex 100 in kerosene as the extractant [30]. Again gold is extracted as an ion-pair, but upon heating the solvent with water, gold metal spontaneously precipitates, presumably through some reductive mechanism involving the extractant itself. Hydrogen reduction has also been demonstrated as an alternative

means of gold stripping [31,32]. None of these processes however are suitable for treating $Au(CN)_2^-$ solutions, particularly very dilute leach liquors, because $Na^+.Au(CN)_2^-$ is not so readily extracted as an ion-pair by solvating extractants compared with $H^+...AuCl^-_4$ and because it is not reductively stripped except by using zinc dust. Thus extraction has relied upon the use of quaternary ammonium extractants, like Aliquat 336, which so strongly anion exchanges with $Au(CN)_2^-$ that until recently no satisfactory method of stripping the gold has been developed (see below). Weak-base tertiary amine extractants (e.g., Alamine 336) unlike their resin counter-part prove to be completely ineffective on their own for extracting $Au(CN)_2^-$ at pH 10. Extraction does not occur until the pH is below 7.

Over the past five years a systematic study on the extraction of $Au(CN)_2^-$ from dilute solutions has been carried out by Miller and co-workers [33-36] and more recently by Riveros at CANMET [19]. In 1984, Miller and Mooiman discovered that by using mixtures of TBP and either primary or secondary amines like Primene JMT or Adogen 283, the basicity of the amine was modified to allow extraction of $Au(CN)_2^-$ at pH 9 rather than pH <7. Significantly, whilst $pH_{\frac{1}{2}}$ values for $Au(CN)_2^-$ extraction shifted by 2-3 pH units (Fig. 2), the $pH_{\frac{1}{2}}$ values for other metal cyanide complexes remained essentially unchanged. This provided a high selectivity of gold over copper and other metals, and easy stripping by pH adjustment (Table 9). For practical applications with low grade liquors, however, this system proved uneconomic due to high soluble losses of organic to the raffinate.

Table 9 - The Effect of Modifier (TBP) on Amine Basicity ($pH_{1/2}$) for Selected Cyanoanions
[(5×10^{-3} M) at 0.05 M Extractant in Xylene [Ref. 34]]

		Adogen 283		Primene JM-T	
Element	Anion	No TBP	50% TBP	No TBP	50% TBP
Cu	$Cu(CN)_3^{2-}$	6.78	7.60	-	-
Cu	$Cu(CN)_4^{3-}$	6.90	7.20	6.10	-
Fe	$Fe(CN)_6^{3-}$	5.66	6.80	5.68	6.72
Ag	$Ag(CN)_2^-$	6.30	8.50	5.10	8.60
Zn	$Zn(CN)_4^{2-}$	7.10	8.45	7.20	8.20
Au	$Au(CN)_2^-$	7.05	9.78	6.05	9.78

Subsequent work aimed at elucidating the mechanism and identifying improved reagents found that a variety of other alkyl-phosphorus esters were effective synergists for the extraction of gold with secondary amines [34]. In particular, tributyl phosphine oxide (TBPO) showed the greatest shift in $pH_{\frac{1}{2}}$ but proved to be the most water soluble [33(b)]. The best compromise between $pH_{\frac{1}{2}}$ shift and low aqueous solubility of reagent was given by a 40% mixture of tri-octyl-phosphate (TOP) plus 0.1 M Adogen 283 in an aliphatic kerosene where soluble losses of TOP and amine were reported to be <20 ppm and <10 ppm respectively [35]. The only major drawback to this system was its tendency to form semi-stable organic phase emulsions, containing about 1% of the aqueous phase. Switching to aromatic diluents to try to overcome this emulsion resulted in lower amine basicity and $pH_{\frac{1}{2}}$ values.

Based upon solvent losses of 30 ppm soluble and 30 ppm entrained, Miller and Sibrell estimate solvent make-up costs to be $0.70 per 1000 gallons of treated clarified solution using conventional mixer-settlers [35]. This amounts to $2/oz Au recovered for a 3 ppm $Au(CN)_2^-$ solution.

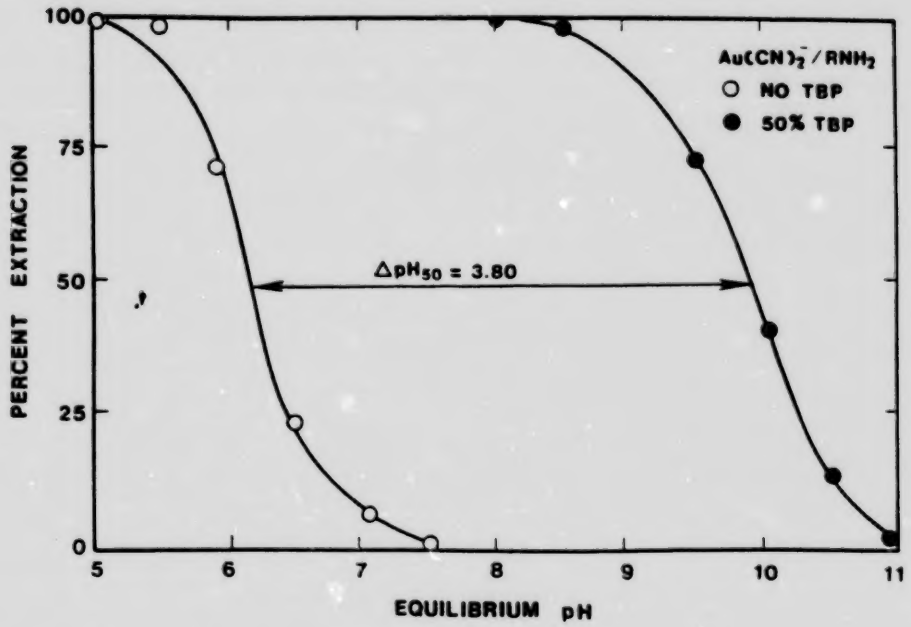


Fig. 2 - The effect of TBP on the extraction of gold (1.0 g/L) from aurocyanide solution by primary amine, Primene JM-T (0.05 M in xylene). [Ref. 34]

Parallel studies by the same group established that the alkyl phosphorus ester solvents, in their own right, extracted aurocyanide but only in the presence of background salts such as NaCN/NaOH. Gold was extracted by an ion-pair mechanism and stripped by water with no effect of solution pH [36]. Of the various extractants tested, dibutyl butyl phosphonate (DBBP) proved to offer the highest distribution coefficient with D ranging from 17-155 according to the concentration of $KAu(CN)_2$; followed by TBP (D = 6-55), trihexyl phosphate (THP) and trioctyl phosphate (TOP). Of particular interest, however, was the high selectivity of these extractants for gold over copper, zinc and iron with selectivity coefficients around 1000. Thus whilst these extracants do not appear powerful enough to extract gold from dilute leach liquors, they may have applications in the processing of scrap gold or gold-bearing residues where selectivity is of the essence and loadings of up to 30 gl^{-1} $Au(CN)_2^-$ are possible.

b) Applied Studies on Clarified Leach Liquors

(i) TBP and TBP/Amine Systems

At CANMET, several solvent systems have been studied using actual clarified gold leach liquors in order to identify problems and prospects for developing a solvent-in-pulp process for gold. Preliminary studies by He [37] used TBP or TBP + Alamine 336 mixtures, and various diluents, to treat a leach solution from the Campbell Red Lake Mine which contained 10 ppm Au, 73 ppm Cu, 33 ppm Zn, 40 ppm Ni, 23 ppm Fe and 820 ppm Na (as CN^- and Cl^-) at pH 10.3. Results were in accord with the reported fundamental studies on synthetic solutions discussed above, and showed that the extraction of gold by TBP alone was sensitive to ionic strength but not pH. The distribution coefficient for gold was about 6 for the untreated leach liquor, but varied with addition of Na_2SO_4 according to the following empirical relationship.

$$D_{Au} = 46.5\ [Na]^{0.58}$$

As soon as diluents were added to TBP, the distribution coefficient D decreased dramatically. Likewise, D decreased significantly with increasing temperature.

With the addition of Alamine 336 to TBP however, D increased from 6 to about 32 in 50/50 mixtures and then decreased to about 4 in pure Alamine 336 for this particular pH liquor. In this case, the mixed extractant was sensitive to pH but not to ionic strength, with D rising from 32 at pH 10.3 to 101 at pH 8.5. Again, diluents had a significant effect on decreasing D, but the effect of temperature was much less compared with TBP alone, reflecting the difference in the mechanism of extraction.

Despite the selectivity of these extractant systems for gold from a liquor containing a 17-fold excess of other metal cyanides, factors such as their limited distribution coefficients, relatively high water solubility and intolerance to dilution with kerosene, preclude their use for dilute aurocyanide solutions.

(ii) Quaternary Ammonium System

More extensive studies by Riveros [19] suggest that quaternary ammonium extractants such as Aliquat 336, Adogen 481 and Adogen 383 are more promising extractants because they extract gold strongly even when diluted to 5% v/v with kerosene. It was found that the previously reported problems of emulsification associated with these extractants [38] could be completely overcome by using aromatic rather than aliphatic diluents, and high molecular weight amines having very low water solubility. Of the various quaternary ammonium extractants tested, a solution of 2.5-10% v/v Aliquat 336 in Solvesso 150 (aromatic kerosene) appeared to offer the best compromise of loading and selectivity.

Table 10 summarises and compares the loading and selectivity factors for this extractant system after a number of stagewise contacts with two clarified leach liquors of widely different composition. After seven contacts with the Campbell Red Lake liquor, the extractant was virtually fully loaded, but after seven contacts with the Teck-Corona Hemlo liquor, only partial loading was achieved. It is predicted that higher loadings of gold will partially displace Cu, Ni and Fe and result in higher selectivity factors.

Whilst the loadings and selectivity factors in Table 10 do not represent true equilibrium or saturation values and cannot be strictly compared, they do point to the superior behaviour of these extractants compared with other extractant systems in terms of their loading and reasonable selectivity. Correspondingly higher loadings of gold were obtained using 10% or 20% Aliquat 336 without any emulsification problems. For example, a 20% Aliquat 336 solution could be loaded to over 3 gL^{-1} Au after successive contacting with Campbell Red Lake liquor. At this loading, the equilibrium distribution coefficient was still around 1000.

Table 10. Loading and Selectivity of 5% Aliquat 336 in Solvesso 150 with Metal Cyanides

Feed	Extraction/Solution Analysis Au	Cu	Ni	Zn	Fe	Au loading Factor	Au/Cu	Au/Ni	Au/Zn	Au/Fe
	(ppm)									
Campbell Red Lake										
Feed	10	85	43	34	31					
5% Aliquat[a]	1800	<50	300	2000	<20	180	>306	26	3	>229
Teck-Corona Hemlo										
Feed	6	4.7	1.5	0	14					
2.5% Aliquat[a]	1350	<50	250	-	200	225	>22	4	-	5

a) after 7 contacts A/O ratio = 40.1;

b) Ratio Au:M in extractant ÷ Au:M in feed

Although the selectivity of the quaternary ammonium functional group is not as high as that offered by the organo-phosphorus esters extractants discussed above, it is significant that the selectivity of Aliquat 336 is much higher than the selectivity of the corresponding resin IRA 4000 having the same quaternary ammonium functional group (Table 7). As discussed by Riveros after comparing the selectivity of various quaternary ammonium type resins and extractants [19], it appears that the selectivity for gold is governed by both the number and the length of the hydrocarbon chain directly bonded to the amino group. Thus quaternary ammonium liquid extractants of the type $R_4N^+X^-$ have intrinsically better selectivity than comparable resins of the type $Resin\text{-}CH_2\text{-}N^+(CH_3)_3X^-$. Even higher selectivity was found in the presence of background salts like $NaNO_3$ because NO_3^- displaces the transition-metal cyanides in preference to $Au(CN)_2^-$ and has little effect on gold loading [19].

iii) Continuous Pilot Tests

Pilot tests by Riveros demonstrated the feasibility of using Aliquat 336 solutions on a continuous aqueous circuit and obtained high gold extraction efficiencies and low soluble organic losses. Because of the unusually high Aqueous:Organic volume ratios of between 300-1000 needed to extract gold from dilute feed solutions of around 5 ppm Au and to load the organic to around 2 gl^{-1}, a novel contactor design was tested and developed (Fig. 3). The aqueous phase was passed continuously through a series of specially designed agitated columns, containing a small volume of organic phase. By proper control, it was possible to maintain an organic-continuous dispersion with settling and separation of the raffinate in the lower part of the column. Periodically, the organic phase was allowed to settle and transfer counter-current through the series of columns. It is claimed that this design allows a wide range of A/O flow ratios to be employed. There is little loss of organic on walls or tubing, or due to splashing, due to the gentle mixing mode and only intermittent organic transfer.

Results of the continuous operation of this system on two different feed solutions over a total period of 115 hours of operation are summarised in Table 11. Using only small volumes of this dilute organic extractant (50 mLs), it was possible to process large volumes of clarified liquors (160-180 litres) and obtain a loaded organic phase containing 2.5 gL^{-1} Au.

Losses of the organic phase over this extended period of time were slight (<10 mLs) and could be attributed to physical handling and wall effects when dealing with small volumes. Although the concentration of dissolved amine in the raffinate was initially high (attributed to soluble low molecular weight impurity amines in the received Aliquat 336) the soluble amine concentration quickly reached an equilibrium value between 3-12 ppm. Ritcey and Ashbrook [27] report that in uranium circuits employing Aliquat 336, initial solubility losses are around 150 ppm, but drop to 10 ppm after 4-5 cycles in circuit.

Table 11. Continuous Extraction of Gold Leach Liquors with Aliquat 336 [19]

	Volume (litres)	Analysis (ppm) Au	Cu	Ni	Zn	Fe	% Au ext'
Feed - Campbell Red Lake	164	10	85	43	34	31	
Extractant - 10% Aliquat 336[a]	0.05	2300	76	557	3820	<30	99
Raffinate a	164	0.2	78	40	19	30	
Feed - Teck Corona Hemlo	180	6	4.7	1.5	0.2	14	
Extractant - 5% Aliquat 336[b]	0.05	2580	82	733	90	<30	91
Raffinate[b]	180	0.1	4.6	0	0	14	

a) A/O ratio in column = 140:1-200:1
b) after 9 cycles with A/O ratio 400:1

Having successfully demonstrated the feasibility of using this extractant for clarified gold cyanide liquors, the other problem faced by Riveros was how to strip the gold as no previous work had successfully identified any feasible practical method. The techniques used to strip strong base resins, namely stripping with 1 M $Zn(CN)_4^{2-}$ or with acidified thiourea [20] had proved to be inefficient for Aliquat 336 [39]. However, it was found that 0.5 M H_2SO_4/0.5 M thiourea solution could strip gold completely if the HCN generated by the acid was completely removed from solution by air-sparging. Over a 10-20 minute period of air sparging with acidified thiourea, about 70-80% of the gold was stripped into the aqueous phase. Complete stripping was achieved by using 3 or 4 contacts of fresh thiourea solution, with air sparging. Furthermore by stripping with 0.5 M H_2SO_4 before adding thiourea, practically all of the base metal cyanide impurities could be scrubbed from the organic phase. Stripping with thiourea also has the advantage of directly regenerating the extractant for recycling and offers various options for recovering gold from thiourea solutions as discussed by Deschênes [40].

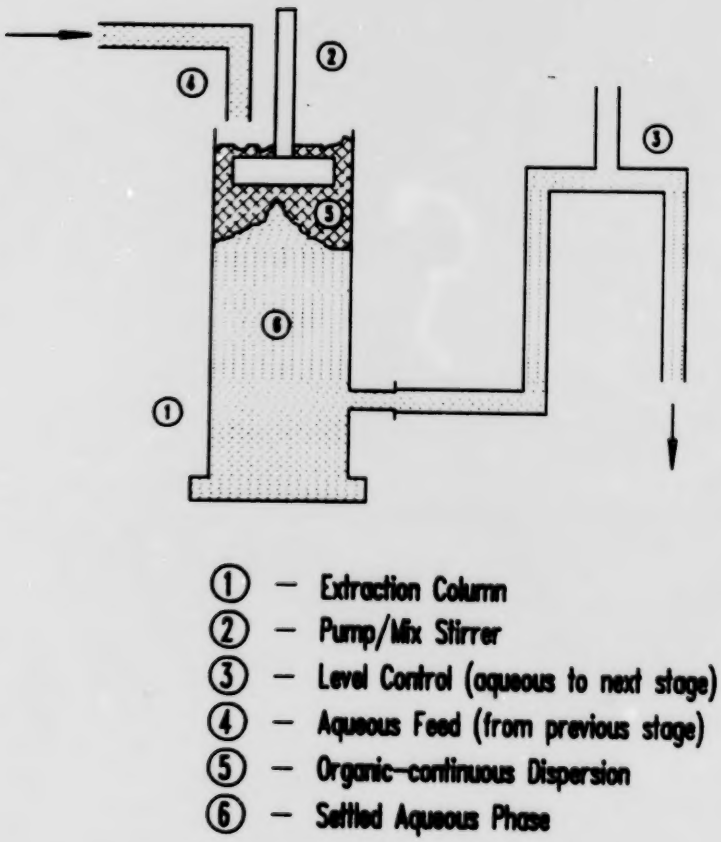

① – Extraction Column
② – Pump/Mix Stirrer
③ – Level Control (aqueous to next stage)
④ – Aqueous Feed (from previous stage)
⑤ – Organic-continuous Dispersion
⑥ – Settled Aqueous Phase

Fig. 3 - Agitation column for continuous solvent extraction of gold.

iv) Conclusions

Research and development over the past three years has focussed its attention on the quaternary ammonium extractants to provide a feasible method of extracting gold from dilute clarified leach liquors. This system is attractive because dilute solutions in kerosene can be employed, thus minimising organic losses; and high loadings and selectivity can be achieved. Significant breakthroughs in technology appear to have been achieved at CANMET in developing a novel contactor system capable of handling large aqueous:organic flow ratios and in overcoming problems in stripping the gold. Thus it should be possible to demonstrate the overall flowsheet and gold recovery circuit on suitable clarified leach liquors in the near future.

Developments in Solvent-in-Pulp

a) Background

Solvent-in-pulp processing was first investigated in the U.S. for the recovery of uranium in the 1950s using mixer-settlers, but this approach was quickly abandoned due to problems of copious cruds (aqueous-solid-organic emulsions) and stable emulsions caused by excessive agitation [8]. Later, more detailed studies by North in the U.K. experienced similar problems with a rotary-film contactor to extract uranium from acidic leach slurries using D2EHPA/TBP or tertiary amines [41]. With D2EHPA/TBP, over 16 litres of the mixed solvent was entrained in the slurry raffinate per ton of solids whilst with amines, half the amine was adsorbed on the silicate solids and stable emulsions were again formed. Meanwhile in Australia, Byerlee found that he could avoid emulsions and minimise losses of TBP-type solvents to around 1.5 litres/ton solid by using columns with gently sloping trays which allowed the pulp to flow without excessive turbulence [42]. This design, however, proved to be very sensitive to flow rates and required close operator control.

In Canada, at Eldorado Nuclear and at the Mines Branch (now CANMET), attention focussed on the application of pulsed plate columns (Fig. 4). The advantage of this contactor appears to lie in its control of droplet size according to the size of holes in the sieve plate, and the amplitude and frequency of the pulse. Droplet size and coalescence varies also with the materials of construction. Organic wettable teflon, for example, produces more elongated droplets than stainless steel, and results in higher losses of entrained organic in the slurry raffinate. In general the gentle agitation conditions provided by pulsing at 30-60 cycles/min at an amplitude of 2-5 cm avoids the formation of emulsions and gives reasonable rates of extraction, but exact optimum conditions vary from system to system.

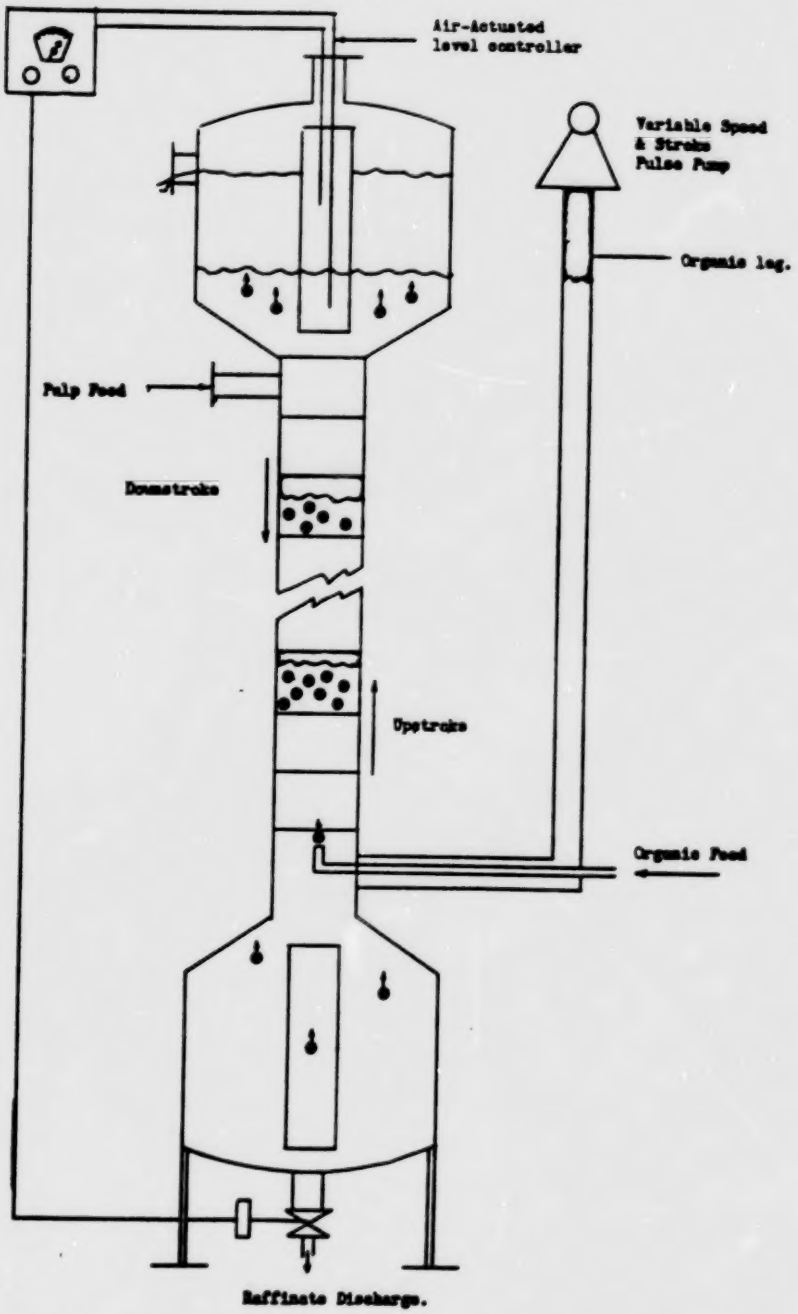


Fig. 4 - Pulse-column used in solvent-in-pulp of Beaverlodge flotation concentrate.

Using sieve plate columns some success has been reported for the extraction of uranium from an acidic pyrite/graphite flotation concentrate, using 5% Alamine 336 tertiary amine [9]. This equipment could accommodate 30-40% pulps at throughputs around 30,000 litres/hour per m^2 of column cross sectional area and gave apparently low amine losses of 0.05 kg/ton solid.

Unfortunately, the presence of 5% w/w graphite caused excessive crud and although this could be readily filtered and washed free of adsorbed amine, the overall effect of graphite is not clear. In any case this represents a typical ore.

b) Tests with Uranium Leach Slurries and Alamine 336

Pilot work with various bacterial leached, atmospheric leached and pressure leached acidic uranium slurries produced mixed results with sometimes high amine losses attributed to adsorption on either colloidal silica or pyrite, or onto the equipment itself (particularly teflon) [8]. Losses of amine also appeared to vary according to the age of the slurry - a factor attributed to hydrolysis reactions causing the formation of colloidal silica and other surface oxides or hydroxides.

From the results of various test runs, it was believed that amine losses on the solid were up to 10 times the soluble loss in the raffinate, depending on the mineralogy of the ore, the pH of the slurry and operating conditions, but it was not possible to quantify or define this further. Preliminary measurements indicated that both the amine losses and amounts of crud formed increased as the average particle size of the pulp decreased. In some cases, up to 50 kg of crud was formed per tonne of dry feed. Analysis of various cruds reveled a disproportionate amount of fines, pyrite, quartz and clay-like minerals relative to the feed composition and found about 0.25% w/w Alamine 336; i.e., (2.5 kg/tonne co-adsorbed). Subsequent tests confirmed that significant amine adsorption took place on pyrite, quartz and muscovite (K, alumino-silicate). Current knowledge on the causes and mechanism of crud formation [43,44] confirm that oxide minerals containing Si, Al, Ca and Fe, hydrolysed compounds and fine precipitates are the major components of cruds in many solvent extraction circuits.

Although much of the amine present in cruds could be recovered by repulping in kerosene and refiltering, subsequent efforts were directed at trying to prevent amine adsorption and

crud formation by adding further flocculants and surfactants to the feed. Reagents such as cellulose-type gums, silicone emulsions and animal and fish protein glues were tested which were widely used in the industry at that time. Most additives resulted in a marginal decrease in amine loss, but in sieve-plate tests, involving 30% slurries contacted with 0.1 M Alamine 336 extractant, the addition of 1 kg fish glue/ton feed reduced the losses of Alamine 336 from 0.55 kg to 0.03 kg/ton feed and eliminated crud formation. Time did not permit any follow-up work or optimization of the dosage of fish glue required.

Clearly a better understanding of the mechanism of adsorption and the role of such additives could assist in identifying more effective reagents. However, the pilot tests did indicate that under the best conditions, using an extractant of 5% Alamine 336 in kerosene containing 5% isodecanol as modifier, solvent losses on 35% w/v pulps could be as low as 0.05 kg amine, per tonne of dry feed, together with some kerosene diluent and isodecanol modifier.

c) Costing

Ritcey et al. [8] have made a preliminary analysis of the solvent-in-pulp and resin-in-pulp processing costs compared with conventional technology using solvent extraction of clarified liquors. Their relative costs (conventional = 100), summarised in Table 12, indicate that processing costs can be virtually halved by avoiding solid-liquid separation. Solvent losses represent over half the overall cost of the SIP circuit but this is more than compensated by the savings involved in eliminating the various liquid-solid separation steps. Thus much higher solvent losses can be tolerated before the cost advantage of direct in-pulp processing is eliminated provided environmental costs are low.

Resin-in-pulp appears to be equally competitive to solvent-in-pulp in terms of cost savings. The main problem with RIP, at

Table 12. Estimated Relative Costs of SIP, RIP and Conventional Processing of a Uranium Leach Slurry [8]
(Conventional Cost = 100)

	Clarified Solutions		Slurries	
Cost Item	SX	Continuous IX	SX[a]	Continuous IX[b]
Solid-Liquid Separation	%	%	%	%
Operating	30	30	-	-
Capital	32	32	-	-
Sand-Slimes Separation				
Operating	-	-	-[c]	5
Capital	-	-	-[c]	5
Solvent Filtration	-	-	1	-
Resin or Solvent Loss	20	3	29[d]	5
Strip Reagents	3	14	3	14
Depreciation[e]				
Solvent/resin	1	2	1	
Capital	8	4	13	12
Labour/Maintenance	6	7	7	7
TOTAL	100	92	54	51

a) based on testwork with 35% pulp density, 40% -200 mesh @ 25,000 litres h^{-1} per m^2 column sectional area
b) based on testwork with 10% pulp density, 100% -325 mesh @ 14,000 litres h^{-1} m^2
c) assuming no significant crud formation
d) assuming 0.05 kg amine, 0.05 kg isodecanol, and 1 kg kerosene loss/tonne feed
e) based on 10 year straight line depreciation

that time, lay with the technical operation of a continuous fluidised bed system which today has been largely overcome.

Advances in RIP technology in the mid-1970s, therefore stifled further efforts in SIP processing in the uranium industry. Nevertheless, the observations and conclusions from this early work as summarised below give some promise for success in applications to gold leach slurries.

d) Conclusions from SIP Testwork with Uranium Leach Slurries

The general conclusions that can be drawn from the tests so far are:

1. Adsorption of solvent onto certain minerals constitutes a major problem requiring further study.
2. Crud formation may represent a problem with certain ores if excessive but can be inexpensively handled if volumes are small.
3. Pretreatment of the ore or slurry with surfactants can minimise adsorption or crud formation and warrants further study.
4. Particle size control may be required.
5. Emulsification and solvent losses due to entrainment in the slurry raffinate can be minimised by gentle agitation and proper control of droplet size or organic interfacial area.
6. Sieve-plate columns, and Byerlee columns [25] are prospective equipment designs for SIP but further design improvements are required.

Solvent-in-Pulp Processing for Gold Leach Slurries

a) Background

Following the conclusion by Riveros [19] that the quaternary amine systems, like 5% Aliquat 336 in Solvesso 150, offered the best prospect for SIP development, studies were initiated at CANMET in 1987 to apply this system to actual pulps from the Campbell Red Lake and Teck-Corona Hemlo Mines [45]. Some of the philosophies, strategy and preliminary observations from initial tests were recently discussed by Ritcey et al [46].

Although previous experience with uranium leach slurries was useful, gold leach slurries differed in several fundamental ways, namely:

1) the pH of the slurry was pH 10 rather than pH 1.5, thus affecting the surface charge and adsorptive properties of the minerals;
2) the extractant required was a quaternary ammonium rather than tertiary amine which was largely unaffected by pH change;
3) the ore minerals were mostly quartz and plagioclase rather than pyrite;
4) the particle size distribution for the gold ores was generally smaller than for uranium ores to liberate the gold for leaching (e.g., 65% - 325 mesh);
5) the concentration of $Au(CN)_2^-$ was 10-100 times lower than $UO_2(SO_4)_2^{2-}$;
6) losses of gold in the slurry raffinate, as well as losses of amine, were critical factors in determining economic viability.

b) Tests with Gold Leach Slurries and Aliquat 336

Early in the testwork with these gold leach slurries, it was clear that the sieve plate contactor was unsuitable because of its tendency to form emulsions and cruds with the finely divided

ores. Thus efforts centered on using a Graesser raining-bucket contactor [27] (Fig. 5) modified with the inclusion of a settling chamber and screw feeder to transport the settled solids underflow through the extraction chamber. The raining bucket mixed the solvent phase with clarified supernatant overflow.

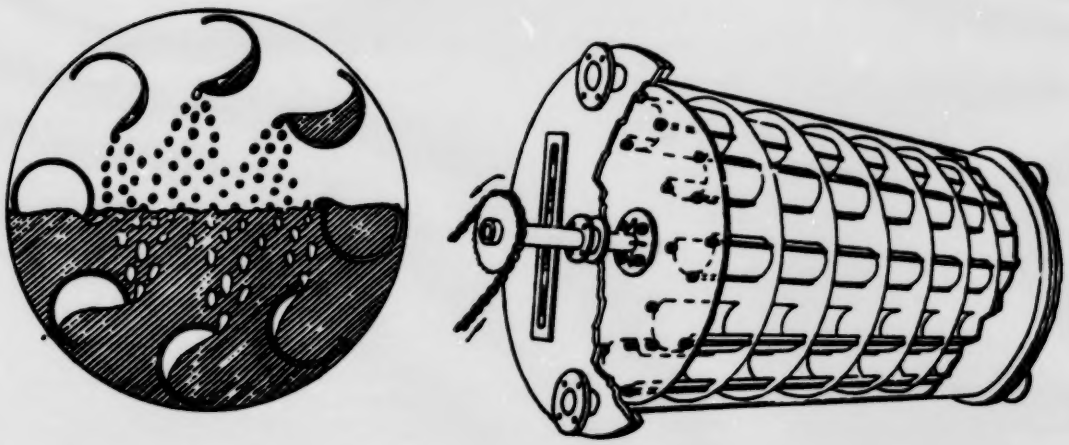


Fig. 5 - Graesser Contactor for S.I.P. [27]

Flocculation of the solids was necessary to accelerate settling and to inhibit crud formation at the aqueous organic interface. Tests by Gao and Molnar [45] established that both the anionic and non-ionic polyacrylamide-type flocculants (e.g., Percol 155, Percol 351) as well as the non-ionic ether copolymers (e.g., Polyox WSR) were effective at dosage rates of 25-50 g per tonne of solids. Each ore though requires individual testing to establish optimum dosage and appropriate flocculant-type [47,48].

With initial tests, the modified pilot Graesser contactor was loaded with 3 litres of 5% Aliquat 336 in Solvesso 150 and used to treat 95 litres of 40% pulp density slurry at a flow rate of 300 mLs min^{-1} and A/O ratio of 400:9. Good phase separation and clear supernatant and organic phases were obtained, but the basic design shown in Figure 5 gave only 30% extraction of the gold from the underflow due to poor mixing of the pulp with the clear supernatant liquor. Furthermore, despite the fast extraction kinetics exhibited by Alamine 336, the rate of extraction of gold from the supernatant liquor was slow (several hours) due to the poor mixing of the aqueous and organic phases when using exceptionally high aqueous/organic volume ratios.

Bench scale tests designed to determine amine losses on the solid due to adsorption [45] gave values ranging from 0.1 - 0.4 kg/tonne (averaging about 0.3 kg/tonne). Various additives such as fish glue, and proprietary surfactants (e.g., Alchem 8A04) appeared to have no major effect on amine losses at dosage rates of 1.5 kg/tonne. However, any small trends could not be identified due to the scatter in the results and the empirical test procedure. In these tests, soluble amine losses in the raffinate were found to be around 50 ppm. This is approximately five-times higher than that reported by Riveros [19], probably due to soluble low molecular weight amine impurities present in the unpurified Aliquat 336.

Conclusions

As discussed by Ritcey [46], the possibility of utilising SIP for gold slurries seems attractive only if appropriate design modifications of the contactor can be achieved to improve mixing and mass transport of $Au(CN)_2^-$ and if a proper understanding of the mineralogy and surface characteristics of the ore leads to inhibition or recovery of adsorbed amine. Further studies are needed to establish the mechanism of amine adsorption and gold losses.

II. INVESTIGATION INTO FACTORS DETERMINING THE VIABILITY OF SIP

Introduction

The mechanisms involved in any solvent-in-pulp process are quite complex as schematically illustrated in Figure 6 and involve chemical, physical and interfacial, as well as kinetic factors associated with the rates and equilibrium of transfer. The transfer, not only of metal values from the slurry to the extractant, but also of the extractant itself from the organic phase to the slurry must be considered. Costs are determined both by organic losses and the efficiency of metal extraction.

Specific factors to be considered in a S.I.P operation and our current understanding of the $Au(CN)_2^-$/5% Aliquat 336 system based on testwork and experience with other SIP systems are summarised in Table 13. Whilst there is a good understanding of the chemical factors, there is still much to be learned, with more quantitative data required on physical and interfacial factors. Kinetic factors would seem to be limited by the need to avoid emulsions/cruds/entrainment and the design of the contactor itself. Careful design is required to achieve optimal rates. Further investigation, therefore, initially concentrated on understanding the physical and interfacial factors and these will be considered in turn.

1) Formation of Emulsions

Stable emulsions can cause significant losses of extractant if entrained within the pulp. The most common oil-in-water type emulsions are stabilised by either anionic or cationic surface active emulsifying agents dissolved in the aqueous phase (I) or by colloids and fine precipitates which have an affinity towards both the organic and aqueous phases and accumulate at the

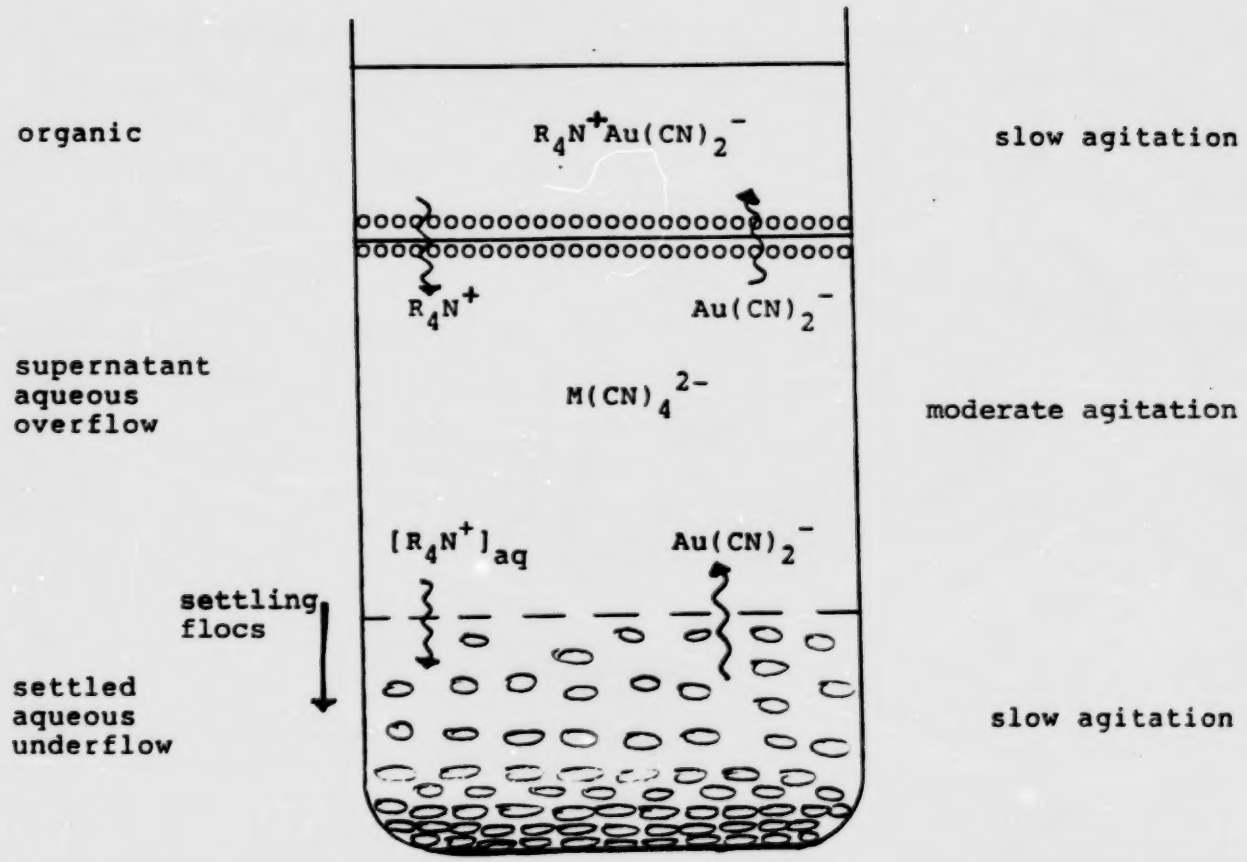


Fig. 6 - Mechanisms involved in the SIP extraction of gold.

interface, (II). In both situations, the oil droplets are prevented from interacting and coalescing; in one case by electrostatic charge, in the other case by the solid phase coating.

Common emulsifying agents include alkyl phosphates and phosphonates, polyaromatic phenols (lignins, humates), and long chain carboxylates, which in alkaline solution have organophilic "tails" and anionic hydrophilic "heads" [49]. Examples of cationic emulsifiers are long chain tertiary amines in acid media and quaternary ammonium salts [50]. Such emulsions can often be broken by pH adjustment and neutralization of the acidic or basic head, except in the case of quaternary ammonium salts, where background salts usually neutralise the charge through ion-pairing.

The effectiveness of these agents appears to be dependent on their solubility in the aqueous phase and their molecular weight. In a recent study of solvent extraction with tertiary amines in acid media, Moyer and McDowell found that lower molecular weight amines such as Adogen 381 exhibited much slower phase disengagement than higher molecular weight amines such as Adogen 383 [51].

In this work it was found that freshly prepared solutions of 5% Aliquat 336 in Solvesso 150 exhibited serious emulsification when shaken with water, and that the amount of amine soluble in the aqueous phase was around 400 ppm. Successive washing of the organic phase with brine solutions gradually reduced the water soluble amine concentration to <30 ppm and simultaneously reduced the emulsification problem. Riveros reported no emulsification

Table 13. Factors determining the performance of a solvent-in-pulp operation

Factor	This system - $Au(CN)_2^-$/5% Aliquat 336
A. Chemical	
i) Distribution coefficient and loading	- High for $Au(CN)_2^-$ in Aliquat 336 [19]
ii) Selectivity over other impurities	- Good selectivity over base metal cyanides [19]
iii) Solubility and distribution coefficient of extractant	- Low for 5% Aliquat 336 ($\leq$10 ppm), but soluble impurities may interfere [19, 45]
B. Physical and Interfacial	
i) Formation of emulsions	- Not serious for clarified liquors using high Mol. wt quaternary amine dissolved in aromatic diluent [19]
ii) Formation of cruds	- Can be serious if fines of clays, pyrite, quartz come in contact with A/O interface [43, 49]
iii) Entrainment of extractant in slurry	- Not serious if droplet size large and no cruds/emulsions
iv) Ability to flocculate fines	- Minimises crud formation. Best flocculant to be determined (cationic, anionic, neutral)
v) Adsorption of extractant onto mineral phases	- Semiquantitative measurements indicate strong adsorption onto pyrite and quartz in acid media [8]
vi) Adsorption of metal values onto mineral phases (especially in presence of flocculants and extractants)	- Adsorption of $Au(CN)_2^-$ in pulp to be determined
C. Kinetics	
i) Rates of interfacial mass transfer of metal values	- Usually fast diffusion control for Aliquat 336 [27]
ii) Degree of mixing of aqueous/organic phases and interfacial area	- Minimal for Graesser contactor; moderate for sieve plate pulse column [27]
iii) Rates of diffusion of entrained metal values from flocculated solids to aqueous supernatant	- Recovery of $Au(CN)_2^-$ to be assessed. Several stages may be required.
iv) Degree of mixing of flocs/solids with aqueous phase	- Minimal for Graesser contactor; good for sieve plate pulse column

with thoroughly washed or recycled Aliquat 336 and found only 10 ppm in the aqueous phase after equilibration with the Solvesso 150 kerosene phase. Thus starting up a SIP operation may give emulsion problems if surfactant impurities are not removed.

The colloids and fine precipitates which stabilise emulsions are generally gels of silica iron and aluminum hydroxides, or colloids of calcium hydroxy phosphates or clays [49,52]. The most effective method of eliminating this emulsion problem is to completely clarify the liquor using flocculating agents or to disperse or peptise the colloid by addition of Calgon (sodium hexametaphosphate).

With cyanide pulps from oxide ores, the most likely problem is the presence of finely divided clays, talc, and the dissolution of silica in alkaline media. Queneau and Berthold recently reviewed the problem of silica in hydrometallurgy [53] and showed that the solubility of amorphous silica increases rapidly above pH 9 from about 100 ppm to >1000 ppm at pH 10.6. Furthermore, the stability of the gel increases above pH 6 due to its increasing surface negative charge. Thus the ageing of clay and reactive silica bearing pulps in alkaline media over a prolonged period could result in third phase emulsification due to the build up of soluble or colloidal silica. The overall conclusion is that emulsions can be a problem but often can be avoided by proper attention to the extractant, aqueous and mineral phases.

2) <u>Formation of Cruds</u>

Cruds or stable aqueous-organic-mineral ternary phases include the colloidal and fine particle emulsifying agents described above, but can include waxy, polymeric or tar-like substances which form at the interface. These occur from the breakdown, polymerization, or oxidation of natural products and certain extractants and modifiers (e.g. oxidation of isodecanol to isodecanoic acid). Over extended periods of time, fungal and

bacterial growths can also give rise to cruds particularly when using aliphatic diluents, rather than the aromatic diluents which act as a bacteriocide [43,54]. Thus with continuous operation of an SIP operation, cruds may appear at a later stage, but proper remedial action can often avoid serious problems.

Cruds can also be regarded as extreme examples of organic adsorption onto the mineral surface giving rise to flotation. Particular tertiary amines and quaternary ammonium salts are recognised collectors for quartz and silicates, as discussed below, and will cause fine particles to float and form stable froths if agitation of the organic and pulp phases is sufficiently intense to introduce air.

In this work, it was found that solubility of Aliquat 336 itself in water was about 250 ppm[+], but even concentrations of 150 ppm readily caused cruds and stable froths upon shaking with -270 mesh quartz, and "oxide" ore from Teck-Corona Hemlo. Flotation of these minerals ceased when the concentration of Aliquat 336 fell below 50 ppm. By contrast, similar solutions of the tertiary amine, Alamine 336, in water at pH 4 gave very little crud (Table 14).

Another observed influence of dissolved amines on the pulp was their effect on the settling rate of the dispersed ore particles. As the concentration of Alamine 336 increased from 50-150 ppm in aqueous solution, settling rates also increased leaving a clear supernatant liquor (Table 14). With Aliquat 336 solutions, however, settling was improved by the addition of 50 ppm but became progressively slower with much dispersion of fines in the supernatant as the concentration increased to 150 ppm. All these factors point to significant adsorption of amines on the mineral surface and emphasise the need to control soluble amine concentrations.

[+] after shake-out with Solvesso 150, Aliquat 336 partitions between the diluent and water and leaves about 5-10 ppm in equilibrium in the aqueous phase.

Table 14. Effect of water soluble Aliquat and Alamine 336 on froth, crud and settling rates of Teck-Corona Hemlo ore* in water at pH 4

a) Aliquat 336

Concentration	Froth	Crud	Settling	Relative Rates+
0	None	None	Slow	4
25 ppm	Slight	None	Quite slow	3
50 ppm	½ cm froth	Yes	Flocs and settles quickly	1
100 ppm	1-2 cm froth	Yes	Moderate, some dispersion	2
150 ppm	2-4 cm froth	Yes	Very slow. Much dispersion	5

b) Alamine 336

50 ppm	None	Slight	Moderate, some dispersion	3
100 ppm	None	Slight	Fast, clear supernatant	1=
150 ppm	None	Slight	Fast, clear supernatant	1=

+ Qualitative ranking for each amine. 1 = best; 5 = worst.

* Mostly quartz and plagioclase ground to -270 mesh.

3) Flocculation and Coagulation of Fines

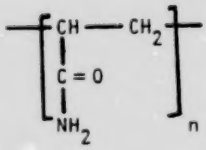
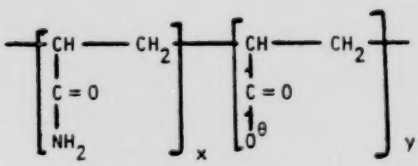
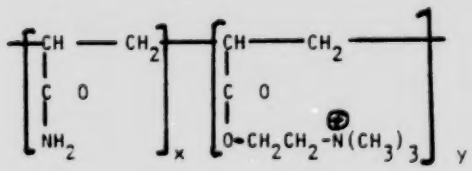
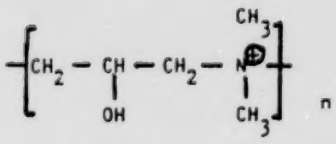
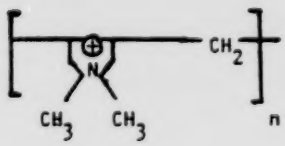
a) Principles

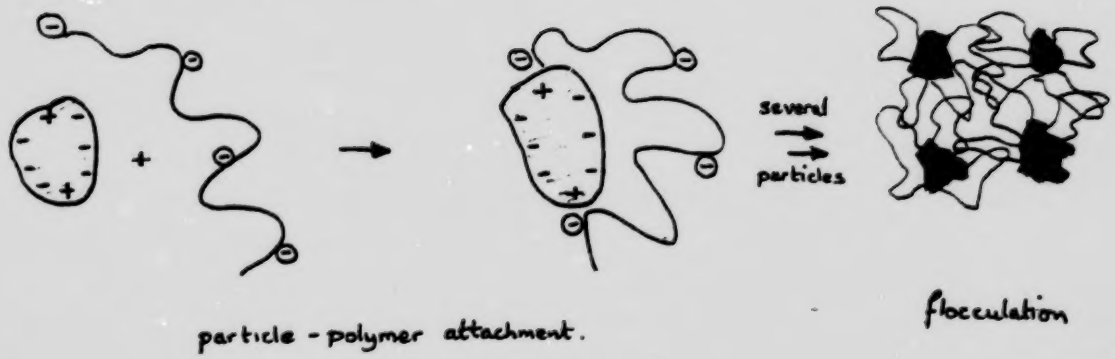
Flocculation is brought about by the addition of high molecular weight materials such as starch, polyethylene oxides, or polyacrylamides (Table 15) which physically bridge between two or more particles to unite them into random three-dimensional loose network structures. Thus the process differs fundamentally from coagulation which involves attraction of particles brought about by lowering the electrostatic surface charge by adsorption of electrolytes of opposite charge such as quaternary ammonium polymers or Al^{3+} (Table 15). Although most mineral particles possess an overall negative surface charge in solution, flocculation can be brought about by neutral, cationic or anionic polymers. However, the porosity and settling characteristics of the floc will differ, and each mineral slurry must be assessed individually to determine the best flocculating agent with regard to its charge and molecular weight, the size and mineralogy of the ore, and the pH of the slurry [47,48,55].

Natural polymers such as starch, glues, gelatins also act as flocculants and coagulants but are of much lower molecular weight and are less effective than the new types of synthetic polyacrylamides now available. They are generally non-ionic, although certain amine containing glues and cellulose derivatives may be cationic, and exhibit variable quality, low floc strength and poor storage characteristics [55].

The mechanism of flocculation is believed to involve attraction of the floc to the mineral surface by hydrogen-bonding and electrostatics, followed by interaction of the polymer loops protruding from each particle to produce a loosely bound porous floc. Thus there is a limit to how much flocculant is required according to the surface area of the mineral, or pulp density of the slurry. Too much flocculant can cause the mineral surface to reverse its charge and lead to dispersion or peptidation.

Table 15. Types of Flocculants and Coagulants

		Mol. wt*
Flocculants		
a) nonionic polyacrylamides		10^6 - 5.10^6
b) nonionic polyethylene oxide	$[CH_2CH_2 - O]_n$	10^5 - 5.10^6
c) anionic polyacrylamides		10^6 - 5.10^6 x/y = 0-20
d) cationic polyacrylamides (tertiary or quarternary ammonium type)		10^6 - 5.10^6 x/y = 0-20
Coagulants		
a) cationic polyamine quaternaries		10^4 - 10^5
b) cationic poly diallyl-dimethyl ammonium chloride		10^4 - 10^5
c) alums	$KAl(SO_4)_2$	Al^{3+}



Depending on the surface charge of the mineral and amount of charge on the polymer itself, the flocculant can be adsorbed tightly onto the surface to give small dense flocs, or can be adsorbed loosely with the polymer chains extended and repelled from the surface to give large fragile flocs (Fig.7) [48]. Because the mineral surface charge varies with pH and is affected by adsorption of other ions from solution, this makes predictions of flocculant performance unreliable.

Table 16 summarises the types of flocculants used in the minerals industry for a wide range of applications with acidic, neutral, or alkaline solutions, and minerals ranging from sulfides to oxides to clays. In some cases, flocculants are used for sedimentation, whilst in other cases, they are used to aid filtration [47,48].

In general, high molecular weight anionic or non-ionic flocculants are more effective at bridging several particles than low molecular weight or cationic flocculants which tend to adsorb on single particles and give small flocs. Hence the most cost-effective and popular commercial flocculants are anionic high molecular weight polyacrylamides which are added to pulps at dosages around 0.025-0.05 kg/tonne solid. However, whilst the large flocs that are produced exhibit the fastest sedimentation rate, they also trap much water or leach solution within its structure. Thus for filtration purposes, where the recovery of solution is important, the other types of flocculant are favoured.

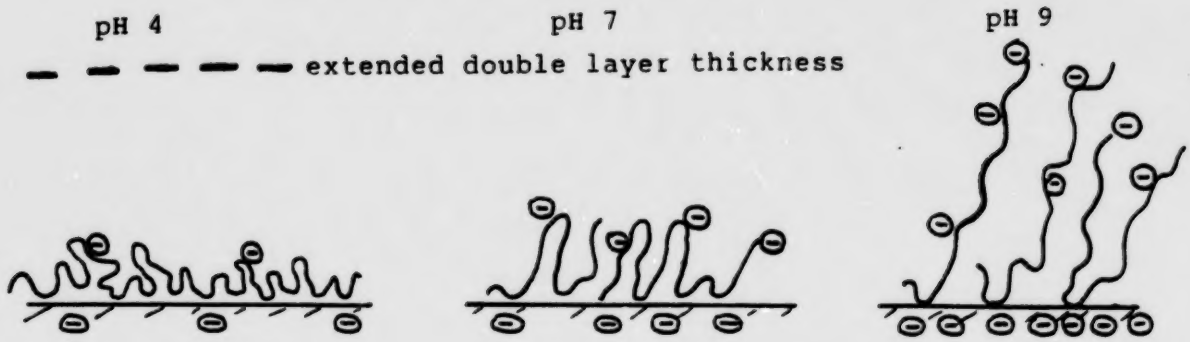
TABLE 16

AREAS OF FLOCCULANT APPLICATION IN THE MINERALS INDUSTRIES [48]

APPLICATION	FLOCCULANT IONIC CHARACTER							
	NON-IONIC	LOW ANIONIC	MEDIUM ANIONIC	MED-HIGH ANIONIC	HIGH ANIONIC	LOW CATIONIC	MEDIUM CATIONIC	HIGH CATIONIC
U/Cu/Co/Ni Acid Leach CCD	H	H				H	H	
U Acid Leach CCF	M	M				M	M	
U Alkaline Leach CCD					H			
U Alkaline Leach CCF					M			
Base Metal Tailings T/C	H	H	H	H				
Pre-Leach ground ores T/C	H	H	H	H				
Coal Tailings T/C			H	H				
Coal Frothed Fines F			/	M				
Electrolytic Zinc-Acid Leach T/C	H	H				H		
Electrolytic Zinc-neutral Leach T/C	H	H	H					
Clayey Coal Tailings			H*					L
Iron Ore Tailings (pH = 11) T/C			H*					L
Iron Ore Concentrate (pH = 11) F								L
Bayer Process red mud T/C					H			
Ni/Co Alkaline Leach T/C	H	H	H	H	H			
Barite/fluorite Tailings		H	H	H				
Highly Colloidal fraction in pulp T/C		H*	H*	H*		H	H	L
Potash Tailings T/C	H	H	H	H				
High pH systems (pH 12) T/C					H			
Phosphate slimes/Tailings T/C		H	H	H				
Sulphate Process TiO_2 Black Liquor T/C							M	M
Sand and Gravel Slurries		H	H					

KEY

CCD - Counter-current decantation
CCF - Counter-current filtration
T/C - thickening/clarification
F - vacuum filtration
H - high molecular weight ($15\text{-}20 \times 10^6$)
M - medium " " (10×10^6)
L - low " " ($<1 \times 10^6$)
* - used in combination with primary coagulant.



Coiled polymer adsorbed mainly in trains due to lack of repulsion with surface; low zeta-potential allows close particle approach and small tight flocs.

Polymer extended existing in loops and tails due to increased repulsion with surface, larger flocs.

High surface charge repels extended polymer from particle; large loops and tails reach far out into solution favouring very large but loose fragile flocs

Fig. 7. The effect of pH on the conformations of anionic flocculants at the kaolin/water interface.

Recent work by Yalcin [56] on the sedimentation characteristics of Cu-Ni mill tailings with a variety of flocculants found non-ionic and cationic polyacrylamides to be more effective than the anionics at pH 7. He also found settling rates to be lowest in acidic media and highest at pH 9. Final pulp densities were typically only between 60-65%, but with agitation of the settled pulp, the density could be increased to around 75%. This emphasises the pulp-specific nature of this work and the need to consider solution entrainment in the floc itself.

For application to alkaline cyanide leach slurries, the high pH and high surface negative charge of most oxide minerals will favour high molecular weight flocculating agents and fast settling flocs. Cationic flocculants tend to be unsuitable above pH 9 because they adsorb too strongly and give small flocs. However, if the leach solution is saline or contains significant

Ca^{2+} and Mg^{2+}, Hunter and Pearse found anionic flocculants also unsuitable because charge neutralization on the mineral again resulted in small flocs [48].

b) Flocculant Studies on Campbell Red Lake and Hemlo Cyanide Leach Slurries

The screening of various anionic, non-ionic, and cationic polyacrylamide and polyethylene ether-type flocculants has been carried out in laboratory tests on two different leach slurries from Campbell Red Lake and Hemlo Mines by Gao and Molnar [45] and Wong [57], respectively. They established the most effective flocculant and those which gave a clear supernatant liquor when added at nominal concentrations of 50 g/tonne solid. A summary of their test results showing the final settled solids volume and the approximate times taken to obtain 50% and 90% of the final supernatant volume is given in Table 17.

Table 17. Screening of flocculants for Campbell Red Lake and Hemlo slurries

Slurry	Flocculant		Dosage	Slurry Vol (mls)		Time to Settle (min)		
	Name	Type	g/tonne	Initial	Final[c]	50%[d]	90%[d]	
Campbell Red Lake[e] pH 10	a) None		-	102	48	75	180	cloudy
	b) Separan MG700	anionic	50	100	53	10	35	hazy
	c) Polyox WSR	non-ionic[a]	50	104	49	15	30	clear
	d) Separan MG205	non-ionic	50	100	50	20	40	clear
	e) Percol 155	anionic	50	102	52	20	40	clear
	f) Percol 351	non-ionic	50	103	51	25	40	clear
	g) Separan M266	cationic	50	103	40	75	180	clear
	h) Alchem 8A4	non-ionic[b]	1500	99	54	100	180	clear
Hemlo[f] pH 10.5	a) None		-	260	120	50	120	cloudy
	b) Percol 156	anionic	~70	260	130	4	15	clear
	c) Percol 1011	anionic	~70	260	122	5	30	clear
	d) Percol 342	non-ionic	~70	260	123	6	20	hazy
	a) None		-	260	150	40	120	cloudy
	b) Percol 155	anionic	~50	260	150	6	40	clear
	c) Separan MG700	anionic	~50	260	150	7	30	clear
	d) Separan MG205	non-ionic	~50	265	150	13	40	hazy
	e) Polyox WSR	non-ionic	~50	275	160	25	50	hazy

a) polyethylene ether type, b) a liquid non-ionic surfactant mixture for dust control and agglomeration.
c) volume of settled pulp d) % of final supernatant volume
e) nominally 45% pulp density f) nominally 43% pulp density

Table 17 shows that the two slurries are sedimented at different rates by the various flocculants. Whilst the Campbell Red Lake slurry is efficiently flocculated by both anionic and non-ionic reagents (particularly Separan MG700 and Polyox WSR), the Hemlo slurry responds better to anionic reagents (particularly Percol 156). Under optimum concentrations and reagent choice, it appears that clear supernatant liquors can be produced after 15-30 minutes of settling time.

In all cases, the final volume of the settled solids is slightly greater in the presence of flocculants than when no flocculant is added, within each series of tests. Settled volumes varied however between each series of tests, presumably because of difficulties in obtaining representative slurries from bulk containers. The volumes indicated that the original slurry densities were between 30-40% based on a typical settled density of about 65%. Thus the concentration of flocculants with respect to the solid were only estimated and no doubt this factor also caused different rates of settling between each series.

In this work, three levels of concentration of flocculant were examined for sedimenting the Hemlo slurry and also the effect of changing from an anionic, to a non-ionic, and to a cationic polyacrylamide-type. The slurry density of the Hemlo sample used was measured and found to be 53% (i.e., 100 mLs pulp contained 69.3 g ore + 84.6 g water). This compares to the nominal 43% produced at the mine, due to the fact that previous sampling of the bulk slurry had preferentially taken more liquor than solids. Flocculants were then added from stock solutions (0.1%) at a dosages of 0.05, 0.10 and 0.25 kg/tonne solid and the tests carried out in the same manner as described by Yalcin [56] in graduated cylinders.

The results of these sedimentation tests, compared in Figure 8, show that the concentration of each type of flocculant must be carefully evaluated. When the concentration is increased from 0.05 to 0.10 and then to 0.25 kg/tonne solid, anionic flocculants become less effective in settling the pulp, whilst

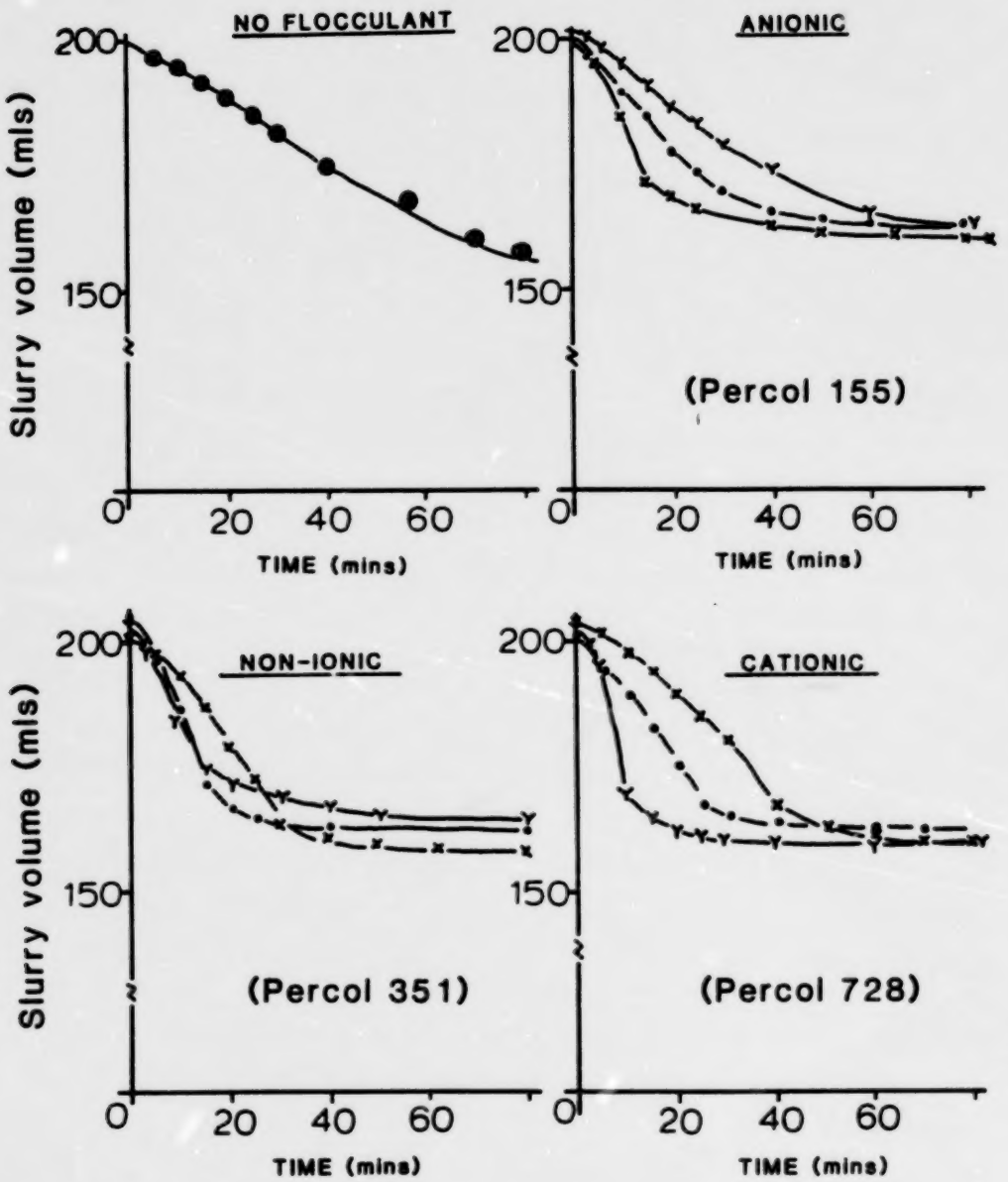


Fig. 8 - Effect of Concentration of anionic, non-ionic and cationic polyacrylamides flocculants on sedimentation rates of Hemlo slurry (53% pulp density).

Key: 0.1% flocculant stock solution added at following dosages with respect to solids X 0.05 kgt^{-1}; ● 0.10 kgt^{-1}; Y 0.25 kgt^{-1}.

cationic flocculants become more effective, and non-ionics pass through a maximum at 0.10 kg/tonne addition. The fastest settling rate was achieved with 0.25 kg/tonne addition of cationic Percol 728 whilst the slowest rate was given with 0.05 kg/tonne addition of the same flocculant.

Although the final settled volume was similar with all three types of flocculant, there was observed, however, a significant difference in the physical nature of the solids. Anionic flocculants at high dosages resulted in a thick semi-solid polymeric floc, whilst non-ionic flocculants produced a more gelatinous custard-like consistency. On the other hand, cationic flocculants produced a small floc which readily redispersed and re-settled upon agitation. This latter type of floc could be easily washed and would seem to be better for SIP applications to permit counter-current washing of the solids in several stages.

c) Conclusions

Although choosing the best flocculant for each slurry is still much of an art, an understanding of the principles and mechanism of flocculation helps to narrow the choice of reagents. High molecular weight anionic and non-ionic polyacrylamide-type flocculants prove to be most effective in settling cyanide leach slurries at low dosage rates. But cationic (quaternary ammonium) derivatives of polyacrylamide reagents give faster settling rates at high dosages of 0.25 kg/tonne solids presumably due to a mixed flocculation/coagulation mechanism and better floc characteristics. Flocs produced with cationic reagents are small and can be readily washed and dispersed whilst flocs produced with anionic and non-ionic reagents are more networked together. Since flocs typically contain 65% solids and 35% solution, it is essential to be able to repulp and resettle flocs easily to recover metal values from the entrained liquor.

4. Adsorption of Solvent Extractants onto Minerals

a) Principles

The adsorption of organic molecules onto a mineral surface is a complex process exploited by mineral processors to selectively separate different types of minerals. Besides the well-known xanthates and dithiophosphates (Aerofloats) used to collect sulfide minerals, the anionic fatty acid carboxylates and long chain alkyl sulfates and sulfonates are used to collect iron ores, chromite and limestone. Cationic amine acetates and quaternary ammonium salts are used extensively to collect and float quartz, silicates and chalcopyrite [50].

The mechanism and factors determining the free energy of adsorption of surfactants was first deduced by Fuerstenau et al in a series of publications in the 1960's and can be considered as a combination of coulombic and specific interactions [58].

i.e., $\Delta G_{ads} = \Delta G_{coul} + \Delta G_{vw} + \Delta G_{CH} + \Delta G_{HB} + \Delta G_{solv} + \Delta G_{chem}$

Where ΔG_{coul} = electrostatic interaction dependent on surface charge (zeta potential) of mineral and charge on surfactant

ΔG_{vw} = Van der Waal interactions between $-CH_2-$ groups in adsorbed alkyl chains

ΔG_{CH_2} = hydrophobic interaction of surfactant with mineral surface

ΔG_{HB} = hydrogen bonding interactions at the surface with surfactant

ΔG_{solv} = free energy changes caused by desolvation in the double layer

ΔG_{chem} = chemical bonding interactions

The specific interactions vary in importance with each system, but in the simplest cases, mainly depend on surface charge (or zeta potential of the double layer), surfactant charge and alkyl chain length. The ΔG_{CH} term becomes important for xanthate flotation of sulfides. The ΔG_{chem} term may be

significant after ageing of certain minerals. Ageing or "conditioning" can produce metal hydroxide layers or gels on the surface which can chemically react with surfactants such as oleates to form insoluble "soaps" [59]. Ion exchange is a more specific chemical reaction which is particularly important with clay minerals.

In general longer chain or higher molecular weight surfactants adsorb more strongly than lower molecular weight homologues [58,50]. Coulombic effects dominate when the mineral and surfactant are of opposite charge, and specific effects dominate when they are of similar charge or when the mineral surface is neutral near its potential of zero charge (pzc).

The pH at which mineral surfaces have zero charge (pH_{pzc}) is specific to each mineral but can vary widely according to its non-stoichiometry or the presence of other ions in solution. Thus each mineral system needs to be experimentally measured [50,58]. Accepted experimental values of pH_{pzc} for a range of common minerals likely to be found in gold ores are listed in Table 18.

Table 18 - Experimental pH_{pzc} of Selected Minerals [50]

Oxides	pH_{pzc}	Silicates		pH_{pzc}
SiO_2	1.8	Biotite	$K(MgFe)_3(AlSi_3O_{10})(OH)_2$	2.1
TiO_2	4.0	Feldspar	$K(AlSi_3O_8)$	4.8
Fe_2O_3, FeOOH	6.6-8.2	Muscovite	$K\ Al_2(AlSi_3O_{10})(OH)_2$	4.0
Al_2O_3	5.0-9.2	Quartz	SiO_2	1.9
MgO	12.4	Olivine	$(Mg,Fe)_2SiO_4$	3.2
Sulfides		**Hydrophobics**		
$CuFeS_2$	1.8	Graphite	C	2-4.2
FeS_2	2.0	Sulfur	S	2.0
FeS	2.0	Talc	$Mg_3(Si_4O_{10})(OH)_2$	1.9
ZnS	2.0			

This table shows that for practically all common minerals, the surface charge will be negative in neutral and alkaline solutions since the pH lies above pH_{pzc} values. Conversely, most minerals carry a positive charge in acidic solutions below pH 2 (commonly used for uranium processing), due to the adsorption of protons. The significant effect of pH on surfactant adsorption is illustrated by goethite, Fe(OOH), which is floated by dodecyl sulfonate anions at pH <6 and by dodecyl ammonium cations at pH >8 [60]. Certain minerals like clays, however, exhibit more complex adsorption behaviour due to lattice defects and ion exchange. Kaolinite displays an overall negative charge, but positive sites occur at edges and defects allowing both anionic and cationic surfactants to adsorb [58]. Furthermore, recent studies by Fuerstenau and Palmer [59], show that the zeta potential also can be significantly affected by the adsorption of inorganic ions from solution. Figure 9 shows that trace amounts (10^{-4} M) of $PbCl_2$, $MgCl_2$, or $FeCl_2$ can reverse the zeta potential of quartz from -ve to +ve over a specific pH range. The change is attributed to the adsorption of $Pb(OH)^+$, $Mg(OH)^+$ and $Fe(OH)^+$ species which predominate in specific pH ranges, and this allows quartz to be recovered by flotation with anionic alkyl sulfonates in alkaline solutions [59]. In the absence of these cationic metal species, the zeta potential for quartz remains negative throughout the pH range.

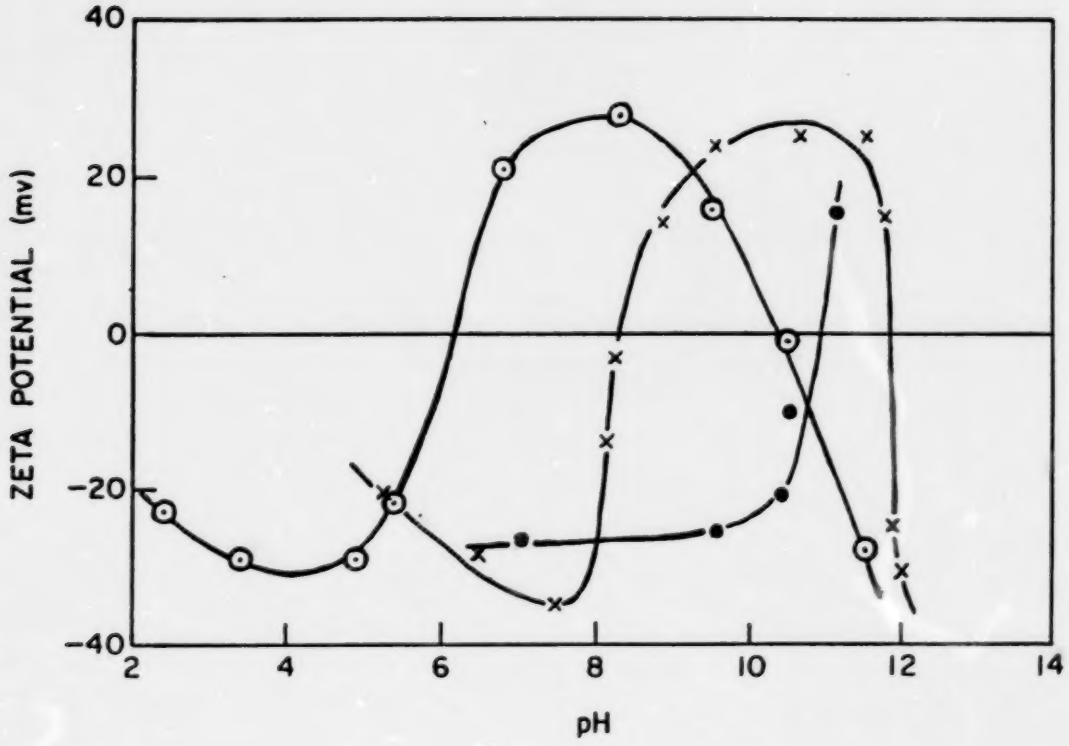


Fig. 9 - Zeta potential of quartz as a function of pH in the presence of 1×10^{-4} M $PbCl_2$ (⊙)
1×10^{-4} M $FeCl_2$ (×)
1×10^{-4} M $MgCl_2$ (●) [Ref. 59]

b) Adsorption of Cationic Surfactants

Most cationic collectors are salts of primary, secondary or tertiary amines, or quaternary ammonium compounds, all with at least 10 carbon atoms. Their solubility and critical micelle concentration (CMC) at which the molecules associate and form micelles in solution, is related to their chain length, chain branching and structure, and this in turn determines their adsorption onto mineral surfaces [61]. As discussed by Ginn [61] and Fuerstenau and Palmer [59] the adsorption of amine is dependent upon solution concentration until the CMC value is reached, whereupon the amount adsorbed remains constant with complete surface coverage. The adsorption isotherms for various long alkyl chain primary amines on alumina shown in Figure 10 [61] illustrate the increasing adsorption and decreasing CMC values associated with increasing chain length. At concentrations below CMC, the adsorption coefficients for tetradecyl and hexadecyl ammonium chloride on alumina (surface area 55-77 m^2/g) appear to be approximately 100, with amine loadings reaching a plateau of 50,000 ppm (0.25 mM/g) at their CMC value of around 500 ppm in water. Other studies with quartz confirm this trend and show that quaternary ammonium salts are even more strongly adsorbed than primary amines at pH 8 [62].

With clay minerals, alkyl ammonium ions ion-exchange readily with Na^+ and Ca^{2+} from the lattice. In a series of studies with montmorillonite clays, Theng et al showed strong adsorption and swelling of the clay with these ions. Again, the strongest adsorption was associated with quaternary ammonium ions of long alkyl chain length [63].

More detailed work by Smith and Akhtar on cationic flotation of oxides and silicates [64], noted that the selectivity of cationic collectors for specific minerals is usually poor and that these collectors usually cause frothing. Almost any oxide and silicate mineral can be collected with these

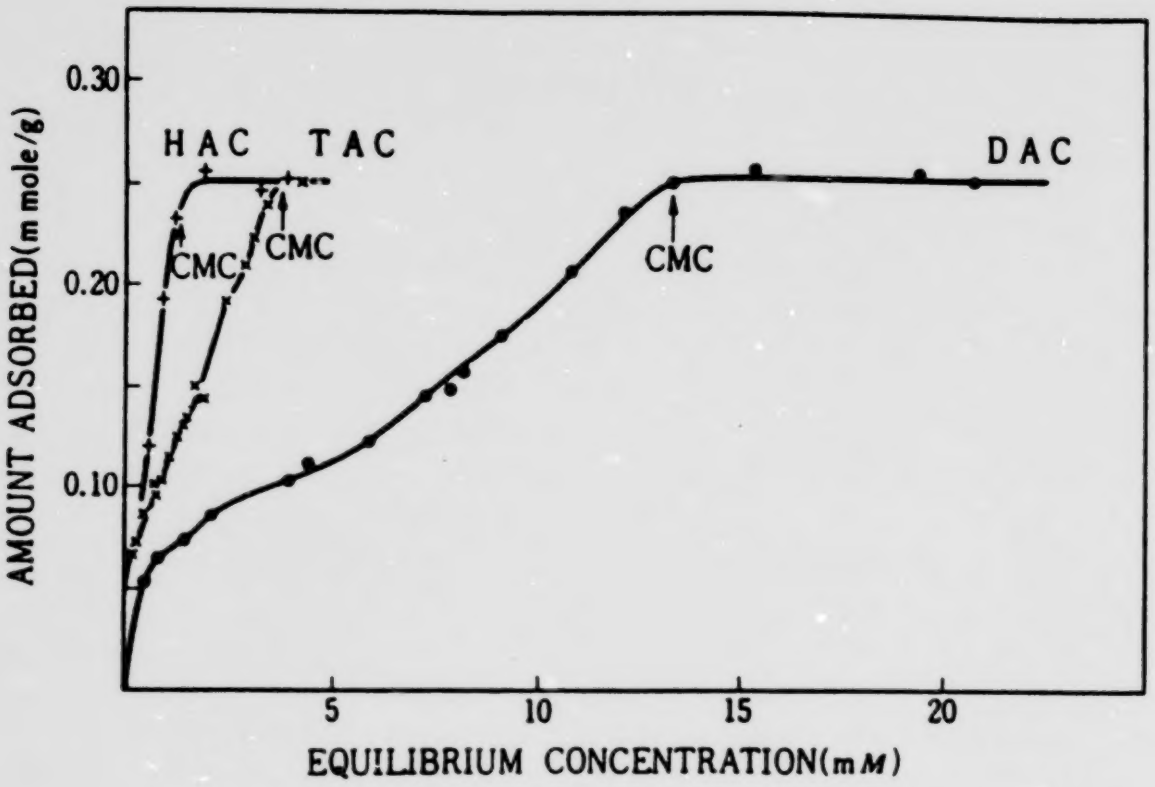


Fig. 10 - Adsorption of long-chain alkyl-ammonium surfactants from aqueous solutions onto alumina (surface area = 55-79 $m^2 g^{-1}$). [Ref. 61]

Key: DAC = dodecylammonium chloride (at 40°C); TAC = tetradecylammonium chloride; HAC = hexadecylammonium chloride; CMC = critical micelle concentration.

cationics over a wide range of pH, even below their pH_{pzc}. Furthermore, they observed that multi-valent anions such as SO_4^{2-} can adsorb on positive sites of the mineral and promote adsorption of cationic collectors. Promotion of adsorption is also achieved by the presence of long chain neutral molecules, such as dodecyl alcohol, which co-adsorb and lower the electrostatic energy of repulsion between adsorbed collector ions. This enhances micelle formation in the double layer [64].

However, certain reagents are recognized to depress adsorption. Besides the specific effects of some cations on reversing the zeta potential of quartz, noted above, several natural starches can act as depressants by creating a hydrophobic mineral surface which may be anionic or cationic according to the type of starch. Corn starch has been used to depress the flotation of iron oxides, and to separate quartz from haematite [64]. However, results are variable and in some cases binary complexes have been identified on the mineral surface involving gums and long-chain amines [64]. The adsorption of starches generally occurs through a relatively weak hydrogen-bonding mechanism with the oxide surface, which is sensitive to the surface condition of the mineral.

Cyanide ion also acts as a depressant in the flotation of pyrite, marcasite, and arsenopyrite with xanthate collectors. Whilst its exact role is not understood, it is believed to complex with metal ions such as Fe^{3+}, Fe^{2+}, Cu^{2+}, etc., and prevent the adsorption of anionic xanthate collectors which utilise these transition-metal cations in their adsorption to the surface [50]. No reports have been found on the effect of CN^- using cationic surfactants.

c) **Conclusions**

Whilst Aliquat 336 has a slightly different structure and higher molecular weight compared to most of the quaternary ammonium-type collectors used in mineral processing, all the theory and evidence from cationic collectors indicate that strong adsorption of Aliquat 336 can be expected on practically all mineral surfaces in alkaline media. In some cases, a decrease in pH, or the presence of metal ions, starches, flocculants, or CN^- may modify the surface charge on the mineral and depress Aliquat 336 adsorption. However, no surfactant has emerged which is likely to displace quaternary ammonium ions, particularly from quartz and clay-like minerals. The low solubility of Aliquat 336

in water is an encouraging feature which promises that adsorption will be limited.

The tertiary amine extractant, Alamine 336, should be less strongly adsorbed than Aliquat 336 because of its structural difference, particularly in alkaline solutions above pH 10, when it is deprotonated and neutral. Whilst Alamine 336 is unsuitable for gold extraction unless mixed with TBP, it is worth investigating its adsorption properties to see if pH changes can effect desorption. This would provide basic data related to the SIP investigation on uranium leach slurries [8], and establish whether the acidic slurry can be rendered free of amine by subsequent washing with alkali.

d) Investigation into the Adsorption of Aliquat 336 and Alamine 336 onto Hemlo Ore, Quartz and Pyrite

i) Introduction

To establish the basic adsorption isotherms and characteristics of Aliquat 336 and Alamine 336, studies were restricted to measuring and comparing the uptake of these amines dissolved in the aqueous phase, onto known weighed amounts of various minerals. The minerals chosen for this study to provide possible contrasts were:

1) dried Hemlo ore (mainly quartz and plagioclase -270 mesh) obtained from drying the gold leach slurry;

2) dried uranium-bearing pyrite concentrate (mainly pyrite - 325 mesh);

3) pure quartz - milled and sized from crystal specimen;

4) pure pyrite - milled and sized from cubic crystals.

Pure crystal specimens were chosen to compare with run-of-the-mill ores in order to test whether impurities or reagents used in the processing operation had any significant effect on their surface properties. Pyrite is a common mineral associated with refractory gold ores, as well as with uranium ores which have already been tested for SIP applications. Because it is hydrophobic, rather than hydrophilic like quartz, it should provide differences in adsorption characteristics.

Surface areas of the ores and sized crystal fractions were determined by BET (N_2 adsorption) measurements using a Quantasorb Surface Area Analyser so that the adsorption data from the various samples could be correlated. Measured areas are presented in Table 19. The finest fraction quartz was talc-like in texture and clearly had a smaller average particle size than the finest fraction pyrite. Significantly the greatest surface area was shown by Hemlo ore and pyrite flotation concentrate, reflecting the greater amount of milling applied to ores in plants, than in the laboratory.

Table 19 - Surface Area Measurements of Samples by B.E.T (N_2)

Sample	Area (m^2/g)	Sample	Area (m^2/g)
Hemlo Ore	1.70	Pyrite Cons.	0.954
Quartz		Pyrite	
-150+200 mesh	0.183	-150+200 mesh	0.076
-200+270	0.236	-200+270	0.208
-270+325	0.369	-270+325	0.415
-325 mesh	1.128	-325 mesh	0.585

Because of practical problems of measurement, analysis, and irreproducibility, as well as fundamental problems of interpretation of data, studies were restricted to the adsorption of amines onto minerals from the aqueous phase, rather than adsorption from the kerosene phase or mixed kerosene-aqueous phases. This represents the ideal situation in SIP, whereby the only mechanism for transfer of extractant from the kerosene phase to the mineral is via dissolution in the aqueous phase. Tests were carried out on the effect of pH and added salts or ions, in an attempt to modify the mineral zeta potential. Finally, the effect of flocculants and kerosene, which co-adsorb on the mineral surface and could modify the properties of the double layer, was examined.

ii) Analysis of Aliquat 336 and Alamine 336

Tertiary and quaternary amines at concentrations between 1-15 ppm were measured directly by spectrophotometric analysis at 410 nm using bromophenol blue as an indicator, according to the method used at CANMET [65]. Aqueous samples (10 mLs) were diluted to 25 mLs with 0.1 M H_2SO_4 then shaken with 10 mLs chloroform, after addition of 1 mL, 0.05% Bromophenol Blue in ethanol. The yellow colour developed in the $CHCl_3$ phase was

analyzed within 10 minutes, due to slow decomposition of the complex, and compared against known standards prepared from stock solutions of 1000 ppm in methanol. Standards between 2-10 ppm gave a linear calibration plot according to Beer's Law, with an absorbance range of 0.10-0.50.

Various related or modified analytical procedures have been described by Cross [66], but most suffer from poor reproducibility or stability. To obtain good reproducibility in this work it was found essential to take care over cleaning glassware, following a consistent technique,and discarding aged solutions. It was also necessary to carry out and correct for blanks by taking standard solutions through the whole procedure, including shake-out, because of adsorption of amine onto glassware. It was found that glassware adsorption could account for up to 10% of amine loss from solution when dealing with small volumes.

iii) Solubility of Aliquat 336 in Water

The solubility of Aliquat 336 in water alone, as determined by adding known μL increments of reagent until the appearance of opalescence or turbidity, was found to be about 150 ppm in pure water, and about 100 ppm in a solution containing 200 ppm NaCN and 2000 ppm NaCl. However, after shaking with a 1:1 volume ratio of Solvesso 150, extraction of the Aliquat left 10 ppm and 9 ppm in the two aqueous solutions respectively, which is close to the soluble amine concentration reported by Riveros in continuous extraction testwork [19] and by Ritcey from plant data [25].

Most of the adsorption studies of Aliquat onto minerals were carried out, therefore, using 10 ppm Aliquat aqueous solutions, but concentrations ranging from 5-50 ppm were used to establish adsorption isotherms.

iv) Adsorption Results

The adsorption of amine onto minerals was established by measuring the decrease in amine concentration in solution after addition of known increments of mineral, ranging from 5-20 gL^{-1}, and equilibrating by shaking for five minutes. Adsorption was found to be rapid (<1 minute) and gave reasonably reproducible equilibrium values (±1 ppm) according to the amount added, after correction for the blank. With large additions of mineral (>20 gL^{-1}), the equilibrium concentration of amine was too low to be accurately determined (<1 ppm) so tests were restricted to small mineral additions to determine the ultimate loading that can be expected in equilibrium with 2-25 ppm Aliquat or Alamine.

a) Aliquat 336 on Hemlo Ore

The adsorption isotherm relating the loading of Aliquat onto the Hemlo ore versus the equilibrium concentration in solution is shown in Figure 11 for three different aqueous solutions; namely pure water, 200 ppm NaCN solution (pH 10) and 200 ppm NaCN solution containing 2000 ppm NaCl.

Despite the apparent scatter of the results, there is clearly strong adsorption of Aliquat which is enhanced in acid and strong salt solutions. The median line of the data from CN^- solutions indicates a logarithmic relationship, i.e., a Freundlich isotherm. Plotting the same data on a log-log scale (Fig. 12), indeed gives a reasonable straight line relationship with a slope of 0.7, but clearly there is slightly less Aliquat adsorption in the presence of 200 ppm NaCN compared with water. There is little difference between water and 200 ppm NaCN solution containing 2000 ppm NaCl, presumably because the depressant action of CN^- is compensated by the enhancing action of NaCl as shown in Figure 11. As discussed above, the exact role of CN^- is not clear, but presumably it forms trace amounts of complex cyanides which modify the double layer and zeta potential. At the 10 ppm concentration in solution, Aliquat would appear to adsorb between 550-800 ppm (0.55-0.8 kg/tonne) onto the ore.

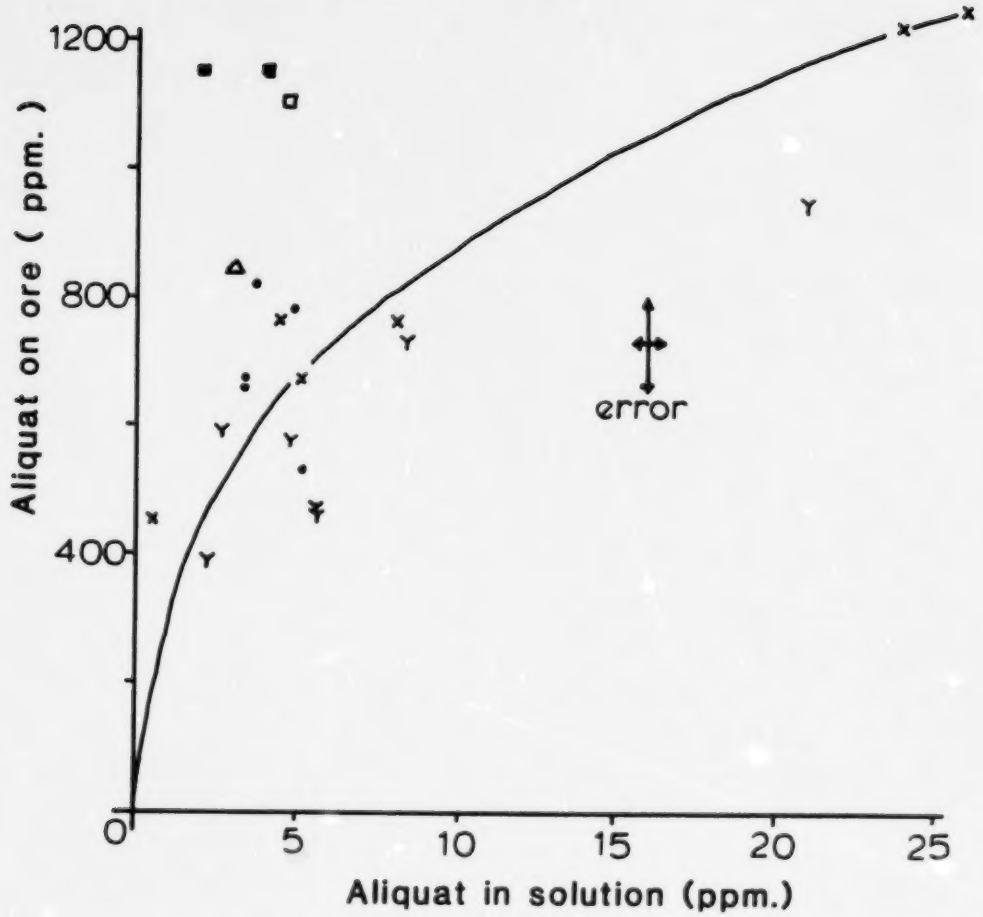


Fig. 11 - Adsorption isotherm for Aliquat 336 on Hemlo ore at 20°C.

Key: Solution are: ✕ water; Y 200 ppm NaCN (pH 10); ● 200 ppm NaCN + 20000 ppm NaCl, △ 200 ppm NaCN + 20,000 ppm NaCl; ■ dil H_2SO_4 (pH 1.85); □ 40 gl^{-1} H_2SO_4 (pH 1.5).

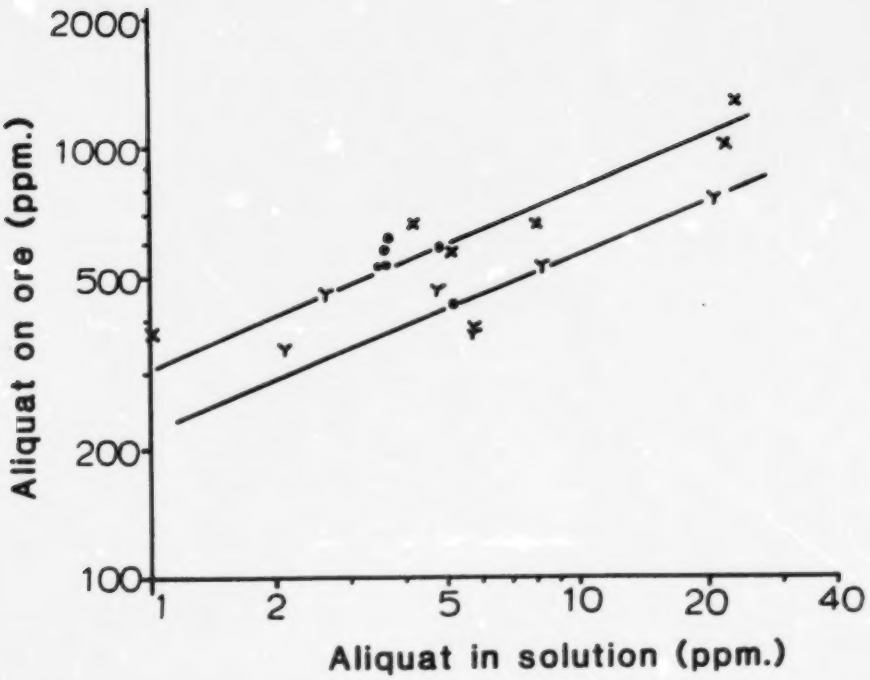


Fig. 12 - Log-log relationship between Aliquat adsorption on Hemlo ore and Aliquat in solution.

Key: ● 200 ppm NaCN + 2000 ppm NaCl, Y 200 ppm NaCN

X water

b) Aliquat 336 and Alamine 336 on Quartz (-325 mesh)

Since Hemlo ore contains predominantly quartz, adsorption of both Aliquat and Alamine were similarly determined using pure quartz (-325 mesh). The solutions studied in this series of tests ranged from 200 ppm NaCN (pH 10) to 1 gL^{-1} H_2SO_4 (pH 3) and 40 gL^{-1} H_2SO_4 (pH 1.5) in order to compare pH effect. This also allows the adsorption of neutral Alamine at pH 10, to be compared to cationic Alamine in acid media.

The results summarised in Figure 13 show similar Freundlich-type isotherms for both amines, with slopes around 0.7. The adsorption of Alamine is slightly stronger than Aliquat in acidic media, particularly at pH 3. Significantly there was no adsorption of Alamine on quartz in CN^- media at pH 10.

Further tests were therefore carried out with quartz in 1 gL^{-1} NaOH (pH 12), to assess the importance of CN^- rather than pH; and also with Hemlo ore to determine its affinity for Alamine. The results of these tests, when combined with previous results, allowed the adsorption of Alamine and Aliquat on quartz and Hemlo ore to be compared with respect to pH, as shown in Figure 14.

Figure 14 plots the measured uptake of Alamine onto the solids, starting with a 10 ppm solution containing 10 gL^{-1} mineral, and shows Hemlo ore to respond in a different manner to pH than quartz. With quartz, there is no Alamine adsorption at pH 10 and at pH 12 in the absence of CN^-, and Aliquat adsorption is depressed slightly at pH 12 relative to the CN^- solution. But with Hemlo ore, although the adsorption of Alamine is only 250 ppm in CN^- solution, the adsorption rises to nearly 1000 ppm at pH 12. Likewise, the adsorption of Aliquat rises at pH 12 to values similar to that in water. Thus whilst CN^- appears to exhibit a depressant effect on Hemlo ore, it exhibits an activating effect for Aliquat on pure quartz. However, since no strict cleaning of the quartz was undertaken, the unusual Aliquat adsorption vs pH relationship could be due to trace impurities modifying the surface charge as observed with trace amounts of $FeCl_2$ (see Fig. 9).

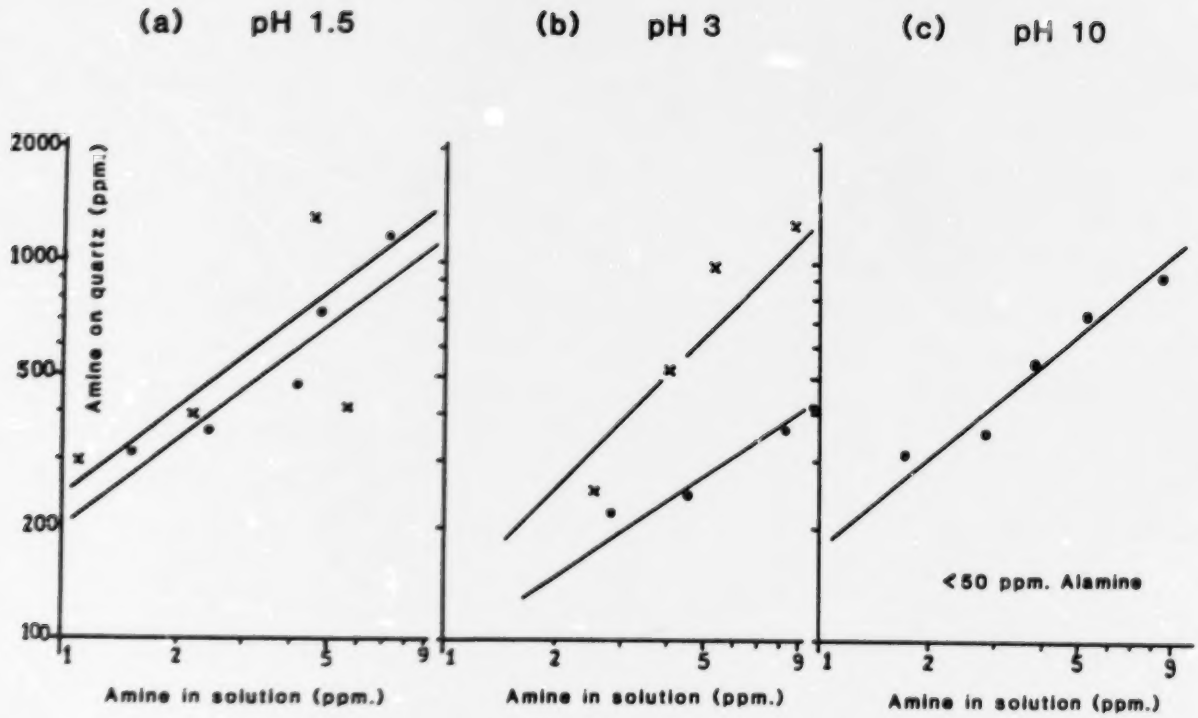


Fig. 13 - Adsorption isotherms for Aliquat 336 and Alamine 336 on pure quartz (-325 mesh) at (a) pH 1.5; (b) pH 3.0; (c) pH 10.

Key: X Aliquat; ● Alamine

(a) 40 gl^{-1} H_2SO_4; (b) 1 gl^{-1} H_2SO_4;
(c) 200 ppm NaCN.

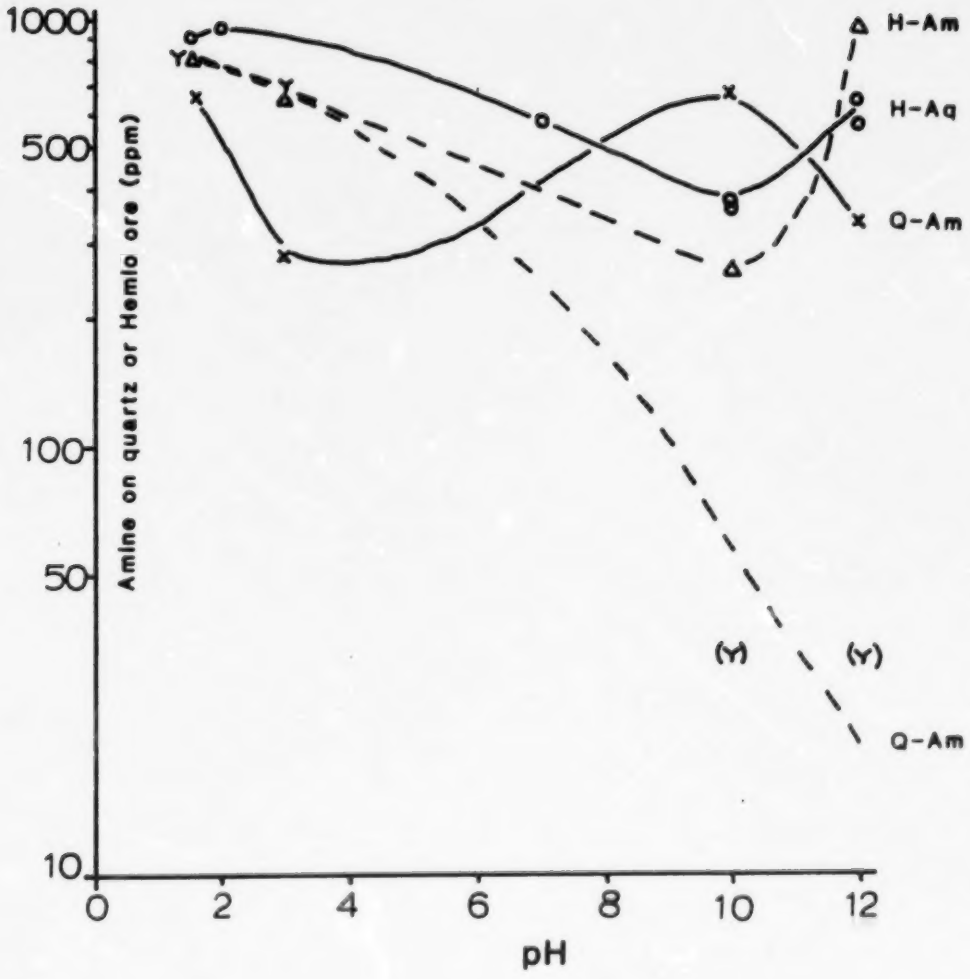


Fig. 14 - Effect of pH on amount of Aliquat 336 and Alamine 336 adsorbed onto quartz (-325 mesh) and Hemlo ore

Key: dashed line Alamine (Am); solid line Aliquat (Aq)

Y,X quartz; Δ O Hemlo ore.
pH 10 (200 ppm NaCN); pH 12 (1 gl^{-1} NaOH)
pH 1.5 (40 gl^{-1} H_2SO_4); pH 3 (1 gl^{-1} NaOH).

Initial Conditions: 10^2 ppm Amine, 10 gl^{-1} mineral.

Finally, to assess the effect of particle size/surface area on the adsorption of Aliquat and Alamine, measurements were carried out with four sized fractions of quartz ranging from -150 mesh to -325 mesh in each of the test solutions ranging from pH 1.5-12. As demonstrated by Figure 15, there is a clear relationship between adsorption and particle size/surface area, particularly with the coarsely ground samples. Adsorption appears to level off somewhat for very fine particles (-325 mesh >1 m^2/g) presumably due to the high charge density restricting further adsorption. In practice, these finely ground particles tend to float and repel each other as to be expected. Whilst the adsorption of Aliquat is around 0.5 $kg.t^{-1}$ on -325 mesh quartz (surface area 1.13 $m^2\ g^{-1}$), it drops to 0.2-0.3 $kg.t^{-1}$ on -150+200 mesh quartz (surface area 0.18 $m^2\ g^{-1}$) in CN^- solution, and even lower at pH 12.

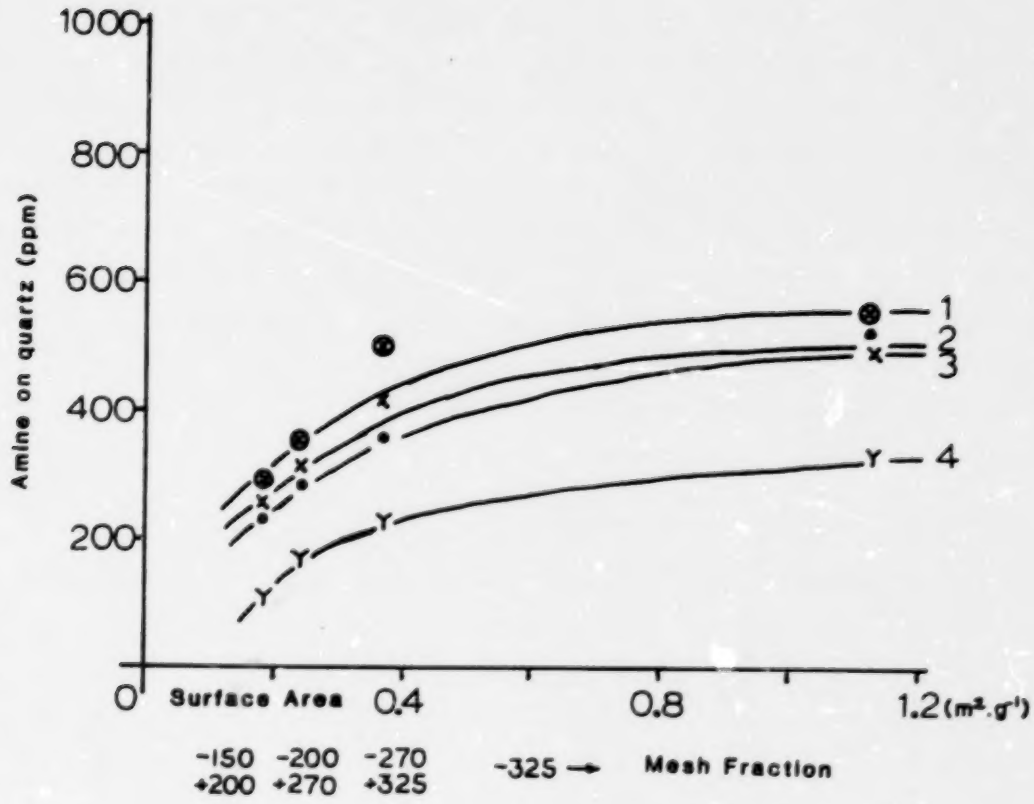


Fig. 15 - Effect of particle size fraction/surface area on amount of Aliquat and Alamine adsorbed on quartz at various pH.

Key:

1	⊗	Aliquat	200 ppm NaCN	pH 10
2	×	Aliquat	40 gl^{-1} H_2SO_4	pH 1.5
3	•	Alamine	1 gl^{-1} H_2SO_4	pH 3
4	Y	Aliquat	1 gl^{-1} NaOH	pH 12

c) Aliquat 336 and Alamine 336 on Pyrite

A parallel series of measurements with Aliquat and Alamine were also carried out using a pyrite concentrate and freshly milled pure pyrite fractions. Figures 16, 17 and 18 summarise the corresponding adsorption isotherm for Aliquat and Alamine on pyrite from 200 ppm NaCN solution, the effect of pH, and the effect of particle size, respectively.

Compared with quartz, the adsorption isotherm for Aliquat on pyrite shows slightly greater adsorption, but with a similar slope. Unlike quartz, however, Alamine adsorbs strongly onto pyrite from 200 ppm NaCN solution with a slope close to 1. This reflects the hydrophobic nature of pyrite strongly interacting with this neutral long chain amine. The effect of pH is, therefore, less with pyrite, with some evidence of an adsorption minimum at pH 10 in 200 ppm NaCN solution (Fig. 17). No significant difference was observed between the pyrite concentrate and the pure pyrite samples with respect to the effect of pH. Thus there appears to be more of a balance between coulombic attractive forces and specific (Van der Waal, etc.) attractive forces in the adsorption mechanism on pyrite. Again particle size/surface area plays a more important role than pH in determining amine adsorption (Fig. 18). The adsorption of Aliquat onto -325 mesh pure pyrite (surface area 0.59 $m^2\ g^{-1}$) is about 1000 ppm or 1 $kg.t^{-1}$ from cyanide solution, dropping to about 250 ppm or 0.25 $kg.t^{-1}$ onto -150 +200 mesh pyrite (surface area 0.08 $m^2\ g^{-1}$).

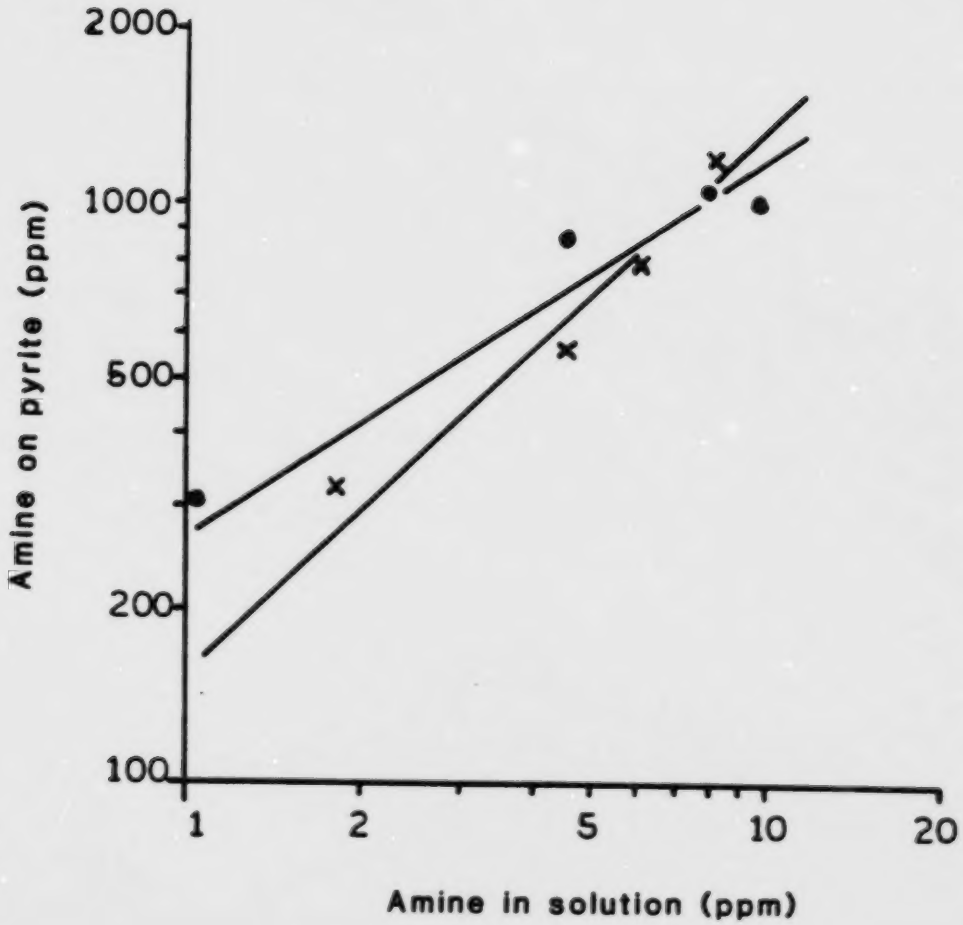


Fig. 16 - Adsorption isotherms for Aliquat 336 and Alamine 336 on pyrite (-200 +270 mesh) from 200 ppm NaCN solution at 20°C.

Key: X Aliquat; ● Alamine

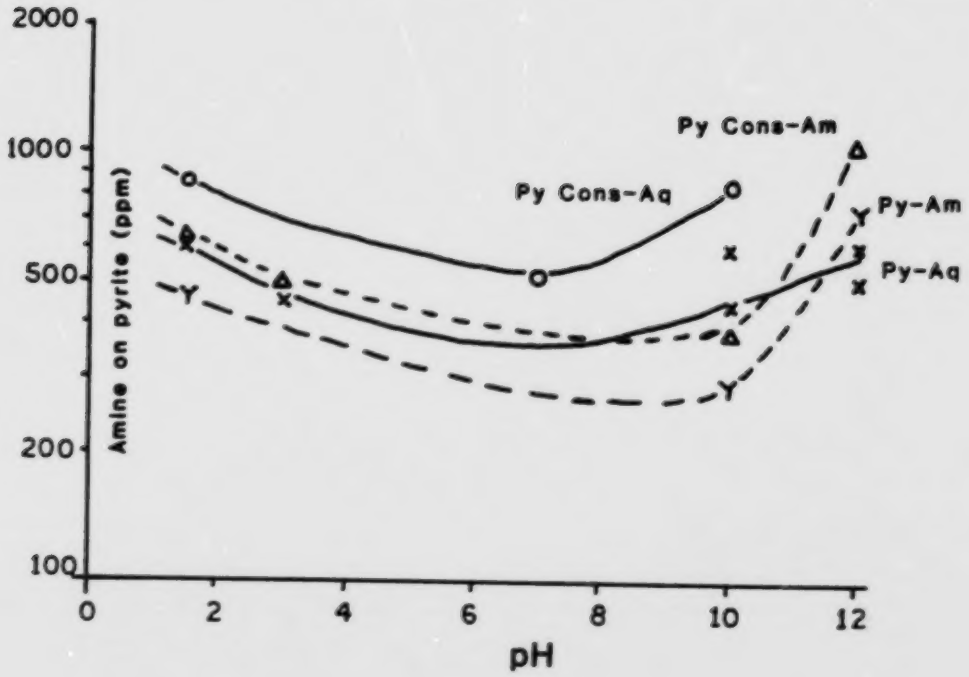


Fig. 17 - Effect of pH on amount of Aliquat 336 and Alamine 336 adsorbed on pure pyrite (-200 +270 mesh) and pyrite concentrate.

Key: dashed line Alamine (Am); solid line Aliquat (Aq)

Y, X pyrite; O Δ pyrite cons.

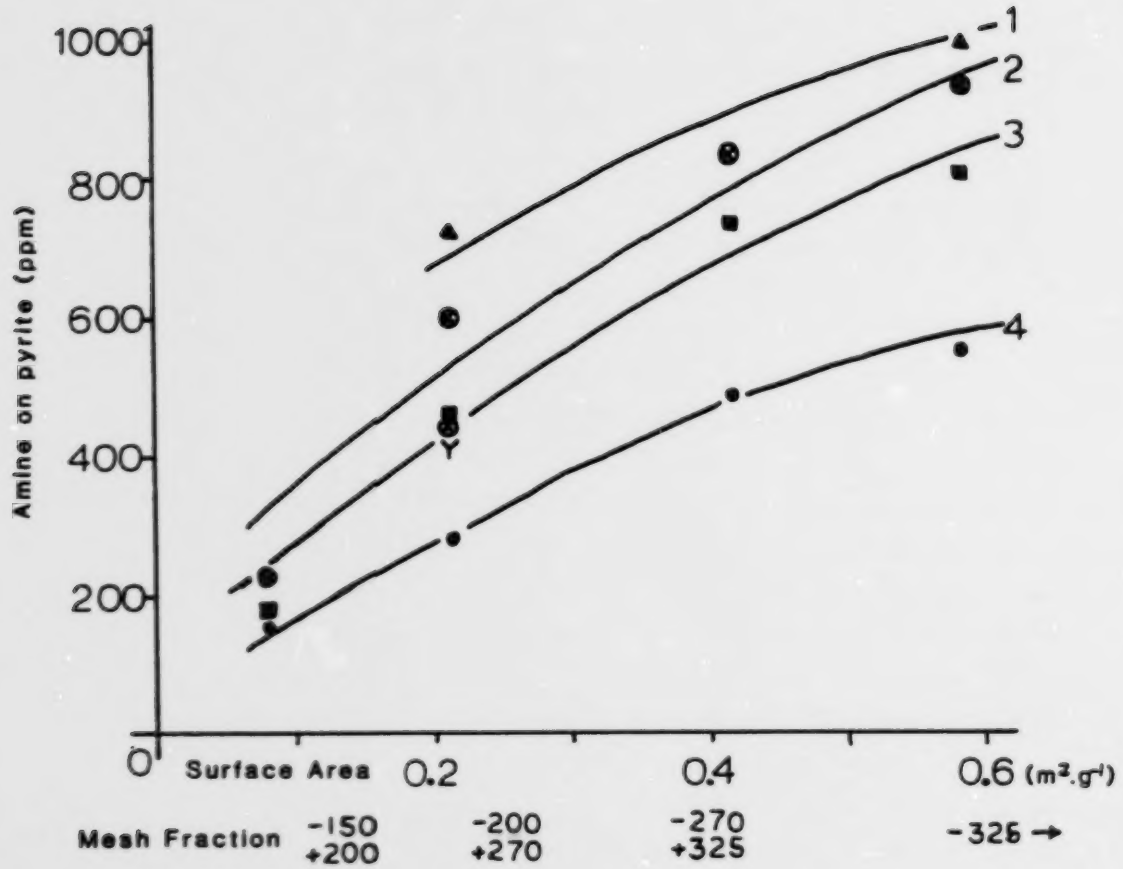


Fig. 18 - Effect of particle size fraction/surface area on amount of Aliquat 336 and Alamine 336 adsorbed on pyrite at various pH.

Key:				
1	▲	Alamine	1 gl^{-1} NaOH	pH 12
2	⊗	Aliquat	200 ppm NaCN	pH 10
3	■	Alamine	40 gl^{-1} H_2SO_4	pH 1.5
	Y	Aliquat	1 gl^{-1} NaOH	pH 12
4	●	Alamine	200 ppm NaCN	pH 10

v) Effect of Possible Pre-treatment Additives on Amine Adsorption

Some tests were made on pre-treating the Hemlo ore and pyrite concentrate with various salts or organic reagents to try to inhibit amine adsorption. In previous work by Ritcey et al [8] and Gao and Molnar [45], sugar, starches, protein glues and kerosene were tried on actual pulps with little success except for fish glue. In this work, $MgCl_2$ was also investigated because it has been shown to reverse the zeta potential of pure quartz at pH 10 (Fig. 9). Most other metal salts though form hydroxides or cyanide complexes in cyanide leach liquors and are unsuitable. With regard to organics, attention focussed on kerosene, fish glue, and both non-ionic and cationic polyacrylamide flocculants. In view of flocculation and mineral processing theory, starches and sugars were not considered likely to exhibit better properties than synthetic flocculants. Likewise anionic surfactants and collectors like alkyl sulfonates, fatty acid carboxylates, humates (aromatic phenols) and anionic polyacrylamides were not considered as any adsorption of these organics would enhance the negative charge on the mineral and lead to greater adsorption of cationic Aliquat by both coulombic and specific interactions.

For each test, small quantities of ore were allowed to pre-equilibrate with the additive in solution prior to addition of Aliquat; but to test the effect of kerosene, the ore was wetted with a kerosene solution in alcohol and dried in order to evenly coat the particles with a kerosene film. Because low pulp densities were chosen for the tests, the weight of additive in solution, relative to weight of ore, was very high - but the concentration in solution is typical for practical pulp densities. Thus any effect of additive will represent the best possible, rather than best practical.

The results of these tests shown in Table 20, show no significant effect of Mg^{2+} and the non-ionic flocculant on Hemlo ore, but some enhanced adsorption of Aliquat after wetting with

Table 20. Effect of solution or mineral pretreatment on Aliquat adsorption from CN^- solution[a]

Solution/Pretreatment	gl^{-1} ore	ppm [Aliquat] In solution Initial	Final	On ore	Remarks
Hemlo Ore					
None	10	9.4	3.6	580	520 from isotherm[b]
None	8	7.8	3.6	530	
CN^-/deionised (no salt)	10	9.4	5.7	370	440 from isotherm[b]
20,000 ppm NaCl	5	7.3	3.1	840	-
120 ppm Mg^{2+}	5	7.3	4.4	580	-
100 ppm kerosene[c]	10	9.4	3.2	620	Flocs solid
1000 ppm kerosene[c]	10	9.3	3.1	620	Readily flocs
100 ppm Fish glue[d]	10	9.7	4.8	490	Poor settling
1000 ppm Fish glue[d]	10	9.4	7.3	240	Very poor settling
100 ppm non-ionic Percol 351[d]	8	7.8	3.6	530	Good settling
100 ppm cationic Percol 728[d]	10	10.2	6.3	390	Some crud
Pyrite Concentrate					
None	10	11.0	2.8	820	-
Pure water	10	11.6	6.0	500	Poorer settling
100 ppm cationic Percol 728	10	11.0	7.4	360	Excellent settling
1000 ppm Fish glue[d]	10	11.0	6.8	420	Very poor settling

a) solution contained 200 ppm NaCN, 2000 ppm NaCl at pH 10 with additives listed.

b) Aliquat on ore given by line of best fit in Figure 12.

c) kerosene added as ethanol solution to dry ore, and redried before adding to solution.

d) ore equilibrated with fish glue or flocculant solution before Aliquat addition.

e) 100 ppm in solution = 10 kg/tonne ore; 1000 ppm = 100 kg/tonne ore.

kerosene. However, about a 30% and 50% decrease in Aliquat adsorption was observed in the presence of 100 ppm cationic Percol 728 and 1000 ppm fish glue respectively. Similar results were observed with pyrite concentrate. Thus it seems that kerosene adsorbs Aliquat and the mineral acts as a solvent unpregnated slurry, whilst cationic flocculants can compete with Aliquat to a limited extent. The exact role or mechanism of fish glue is not understood. Presumably it contains proteins with amine side chains and positive sites, but it also acts to disperse the solid rather than flocculate like cationic polyacrylamides. The high concentrations of fish glue required (2 $kg.t^{-1}$ solids) and the poor settling characteristics of the slurry discourage further investigation. Although Percol 728 gave good settling characteristics, the amount used was 10 times greater than normally used for flocculation with regard to the amount of solid present, making this uneconomic.[+]

The previously reported success of kerosene in decreasing amine losses in pulp [8] would appear to be a result of its ability to flocculate the solids, thus inhibiting emulsions or entrainment. But the manner of contacting kerosene with slurry is also critical. Previous work with sieve plate pulse columns provided mixing without shear and emulsions, but when a 50% pulp density slurry was vigorously shaken with excess kerosene (A:O = 20:1) an emulsion was immediately formed with much crud.

[+] Cost of Percol flocculants /$10/kg

vi) Conclusions

The general conclusions drawn from all the adsorption studies with aqueous solutions can be summarised as follows:

1. Adsorption of Aliquat and Alamine onto silicate and pyrite minerals follows a Freundlich-type Adsorption Isotherm dependent on the solution concentration and surface area (A) or particle size of the mineral.

   i.e., $[\text{Amine}]_{\text{mineral}} = K.A.[\text{Amine}]^{n}_{\text{solution}}$

   For solution concentrations between 2-20 ppm, n = 0.5-0.8 and K ranges between 100-400.
2. Adsorption on pyrite per unit surface area is about double that on quartz.
3. Adsorption is dependent on pH, high concentrations of background salts and CN^-. It is highest in acidic solutions and lowest in CN^- solution at pH 10.
4. The mineralogy of the ore and its impurities affect adsorption properties significantly.
5. Neutral Alamine (pH >10) adsorbs strongly on pyrite but not on quartz.
6. Cationic surfactants and flocculants can depress Aliquat adsorption by up to 50% but only when relatively high concentrations are used.
7. High concentrations of amine in solution or small particle size of ore result in flotation, frothing and crud formation.
8. Typical loadings of Aliquat onto finely ground silicate and pyrite ores (>0.5 $m^2\ g^{-1}$ surface area) can be predicted to be around 400 ppm (0.4 kg/tonne) and 800 ppm (0.8 kg/tonne) respectively after equilibrating with cyanide solutions containing 5-10 ppm Aliquat.

9. Best conditions for minimising adsorption appear to be coarsely-ground ore (+150 mesh) with excess free CN^- and cationic flocculants.
10. Lowest achievable levels of adsorption appear to be 250 ppm (0.25 kg/tonne).

5. Adsorption of $Au(CN)^-_2$ onto Pulps

Certain ores containing carbonaceous material are known to adsorb $Au(CN)^-_2$ and inhibit adsorption onto activated carbon [67]. As a result, the carbon-in-leach process was specifically designed to try to overcome this effect, by having activated carbon present in the leach solution to preferentially adsorb $Au(CN)^-_2$ before it became adsorbed on other carbonaceous material [68]. The exact nature of the carbonaceous material causing strong adsorption of $Au(CN)^-_2$ is not known, but the presence of organic flocculants and in particular Aliquat 336 on the mineral surface is likely to provide a mechanism for adsorption.

Attempts by Abotsi and Osseo-Asare [69] to identify the carbonaceous fraction from actual ores have met with limited success. Therefore in their most recent work [70] they examined the effect of model surface active organic compounds on gold adsorption by a carbonaceous ore. In particular, they found significant gold uptake onto the ore after addition of Aliquat 336, 0.01 g/kg (100 ppm) and slight uptake after addition of dodecylamine (DDA) and sodium dodecyl sulfate (SDS). By contrast, dinonyl naphthalene sulfonic acid (I) (HDNNS) and pretreatment with hexane had an opposite effect. With the addition of 100 ppm Aliquat 336 to the ore (dispersed in a hexane solution) about half of the gold in the ore was retained by the pulp after leaching [70].

I = (HDNSS)

These results are not surprising since in cyanide solutions, Aliquat 336 is cationic whilst SDS and HDNNS are anionic and DDA neutral. Thus the influence of the adsorbed additives was attributed to electrostatic and chemical interactions with $Au(CN)^-_2$.

In this work, tests were carried out on Hemlo slurry in which the concentration of $Au(CN)^-_2$ was measured before and after the addition of known amounts of anionic, non-ionic and cationic polyacrylamide flocculants and after addition of standard amounts of Aliquat 336.

Initial measurements of $Au(CN)^-_2$ in the leach slurry which had been stored for over 1 year, however, indicated <0.1 ppm Au. Subsequent tests then showed that this "aged" pulp had lost free CN^- through oxidation or complexation and had a pH of only 8.4. After adding 200 ppm NaCN and readjusting the pH to 10.5 the concentration of $Au(CN)^-_2$ increased to 3.4 ppm. It is proposed that the "aged" pulp, in the absence of free CN^- contains NH_4^+ and cationic hydroxide species such as $Ca(OH)^+$, $Ni(OH)^+$, which would adsorb on the mineral surface (see Fig. 9) and hence ion-pair with $Au(CN)^-_2$. Thus it seems that gold losses to the pulp can occur through inorganic as well as organic adsorption mechanisms.

The results of flocculant and Aliquat additions to the cyanide adjusted pulp at typical and excess plant concentrations are given in Table 21. This table shows that none of the polyacrylamide flocculants have any significant effect on $Au(CN)^-_2$ adsorption even at a concentration of 0.25 kg/tonne solids, which is 5 times normal recommended levels. However, similar additions of Aliquat 336 cause a marked decrease in $Au(CN)^-_2$ in solution. Addition of 50 ppm Aliquat to the slurry (=0.10 kg/tonne solid) resulted in half of the $Au(CN)^-_2$ being adsorbed whilst >100 ppm Aliquat (0.20 $kg.t^{-1}$) resulted in complete loss of gold to the pulp. Measurements of amine concentration remaining in the solution confirmed that all the Aliquat had been adsorbed onto the pulp.

Table 21. Adsorption of $Au(CN)_2^-$ onto Hemlo pulp* in presence of flocculants and Aliquat 336

Additive	Conc. w.r. to slurry ppm	Conc. w.r. to solid $kg.t^{-1}$	$Au(CN)_2^-$ ppm		
None	-	-	3.4 ±0.1		
Anionic Percol 155	25 ppm	0.05	3.3		
	50	0.10	3.10[a]		
	125	0.25	3.05[a]		
Non-ionic Percol 351	25	0.05	3.2		
	50	0.10	3.2[a]		
Cationic Percol 728	25	0.05	3.2		
	50	0.10	3.2[a]		
	125	0.25	3.05[a]		
			Before	After	[Aliquat]
Aliquat 336	5	0.01	3.3	3.3	<0.2 ppm
	10	0.02	3.2	3.1	<0.2
	25	0.05	3.2	2.5	<0.2
	50	0.10	3.2	1.6	<0.2
	100	0.20	3.2	0.5	<0.2

* Hemlo slurry adjusted to 200 ppm NaCN, pH 10.5, Pulp density = 53%.

a) Slight decrease in measured $Au(CN)_2^-$ attributed to dilution factor caused by addition of 0.1% stock flocculant solution.

Since previous studies have shown that pulps can adsorb up to 0.4 kg Aliquat/tonne, the adsorption of $Au(CN)^-_2$ onto the pulp must be considered as the most serious factor challenging the applications of SIP to gold leach slurries. Low losses of $Au(CN)^-_2$ could only be achieved if the rate of transfer of $Au(CN)^-_2$ to the extractant was much faster than the rate of transfer of Aliquat to the pulp.

6. Rates of Diffusion of $Au(CN)^-_2$ and Aliquat 336 Between Aqueous and Kerosene Phases

In a well-mixed system like mixer-settlers the rate of extraction of $Au(CN)^-_2$ into the Aliquat 336-kerosene phase is fast (<1 minute) and diffusion controlled. But as reported by Gao and Molnar [45] extraction may take >1 hour if the aqueous:organic phase ratios are high and stirring of the aqueous phase does not disperse the organic. For SIP applications mixing is limited by the need to prevent solids contacting with the organic interface, and organic droplets transferring to the settled solids. Vigorous mixing results in emulsions, cruds and rapid transfer of organic droplets to the pulp, therefore it is preferable to maintain a quiescent interface whilst stirring the aqueous and organic phases as much as possible.

Such conditions were used in fundamental studies on the kinetics of extraction of $CuCl^{2-}_4$ by Aliquat 336 in xylene recently reported by Fuerstenau et al [71]. Their cell, shown in Figure 19, allowed both the aqueous and organic phases to be stirred at defined rates up to 100 rpm without disturbing the interface.

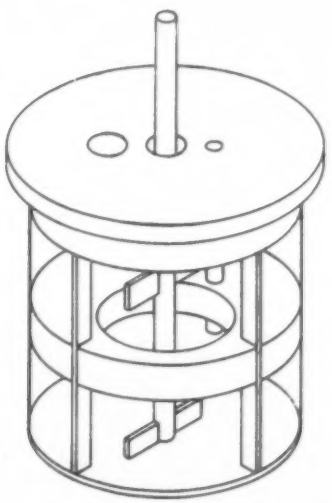


Figure 19. Diagram of the cell used by Fuerstenau et al [71] in the extraction of $CuCl^{2-}_4$ by Aliquat 336.

The results of their work showed that the kinetics of extraction was first-order with respect to Aliquat and $CuCl_4^{2-}$ concentration. At relatively low stirring speeds the rate of extraction was dependent on stirring, indicative of mass-transport control to the interface, but at higher stirrer speeds (>80 rpm) stirring had no further effect. The low enthalpy of activation and other factors suggest that under well-stirred conditions the rate is determined by ion-pair formation at the interface; i.e., $CuCl_4^{2-}$ ... $[R_4N^+]$. Using this cell, the initial extraction rate of the $CuCl_4^{2-}$ species (2.10^{-5} M) with 5% Aliquat 336 was found to be about 4.10^{-6} M Cu per hour per cm^2 interfacial area at 25°C when stirred at 90 rpm. Similar rates and mechanisms are expected for the $Au(CN)^-_2$ - 5% Aliquat 336 system.

In this work, time did not allow construction of a proper cell so a preliminary study of the rate of $Au(CN)^-_2$ and Aliquat transfer was measured in beakers between an aqueous phase (300 mLs) containing initially 7.0 ppm $Au(CN)^-_2$ ($3.5.10^{-5}$ M) and a kerosene phase (150 mLs) containing 5% v/v Aliquat 336. The organic phase was left undisturbed, whilst the aqueous phase was stirred with a magnetic stirrer, as fast as was possible without creating a vortex and dispersing the organic (~100 rpm). This would approximate the best conditions to operate a S.I.P contactor without mixing the phases, provided the flocculation was efficient or particle-size was sufficiently great to prevent dispersion.

Figure 20 shows the % $Au(CN)^-_2$ remaining in the aqueous phase (relative to its initial concentration) and compares the % Aliquat appearing in the aqueous phase (relative to its final equilibrium value) over the same time period. When "as-received" Aliquat 336 was first used, the aqueous Aliquat concentration at equilibrium, after 24 hours stirring was 450 ppm. But after 6 successive washings with brine solutions, the equilibrium concentration had dropped to 35 ppm. As Figure 20 shows, despite the change in Aliquat concentration entering the aqueous phase the relative rate of Aliquat transfer from the kerosene phase to

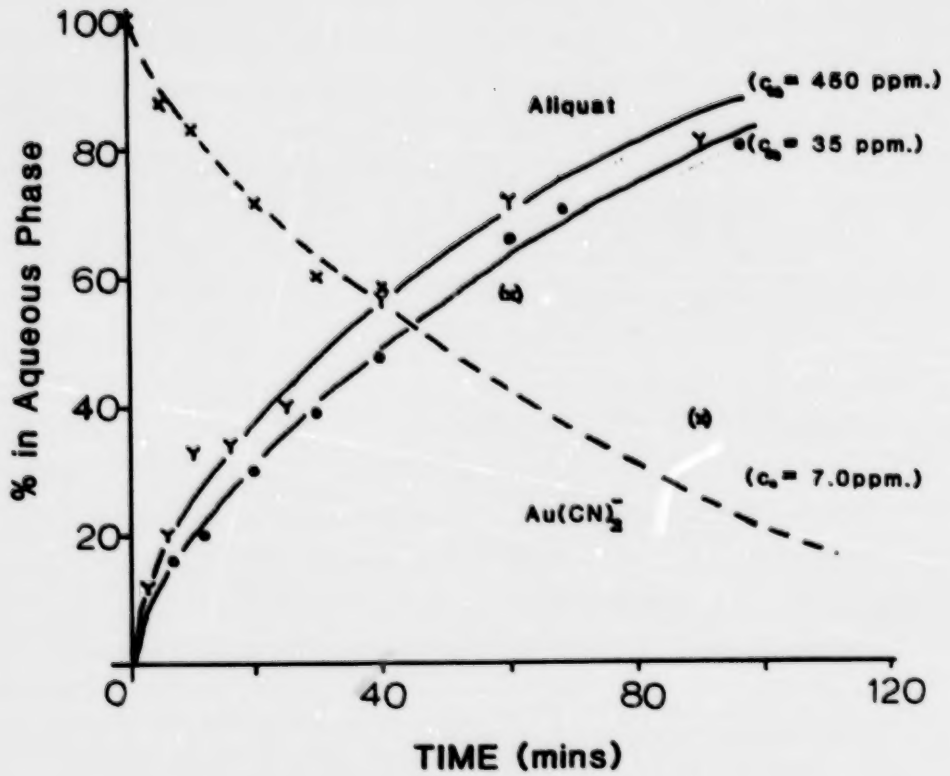


Fig. 20 - Fraction of Aliquat 336 and $Au(CN)^-_2$ in aqueous phase (relative to initial or final value) due to transfer between water and kerosene in gently stirred cell at 20°C.

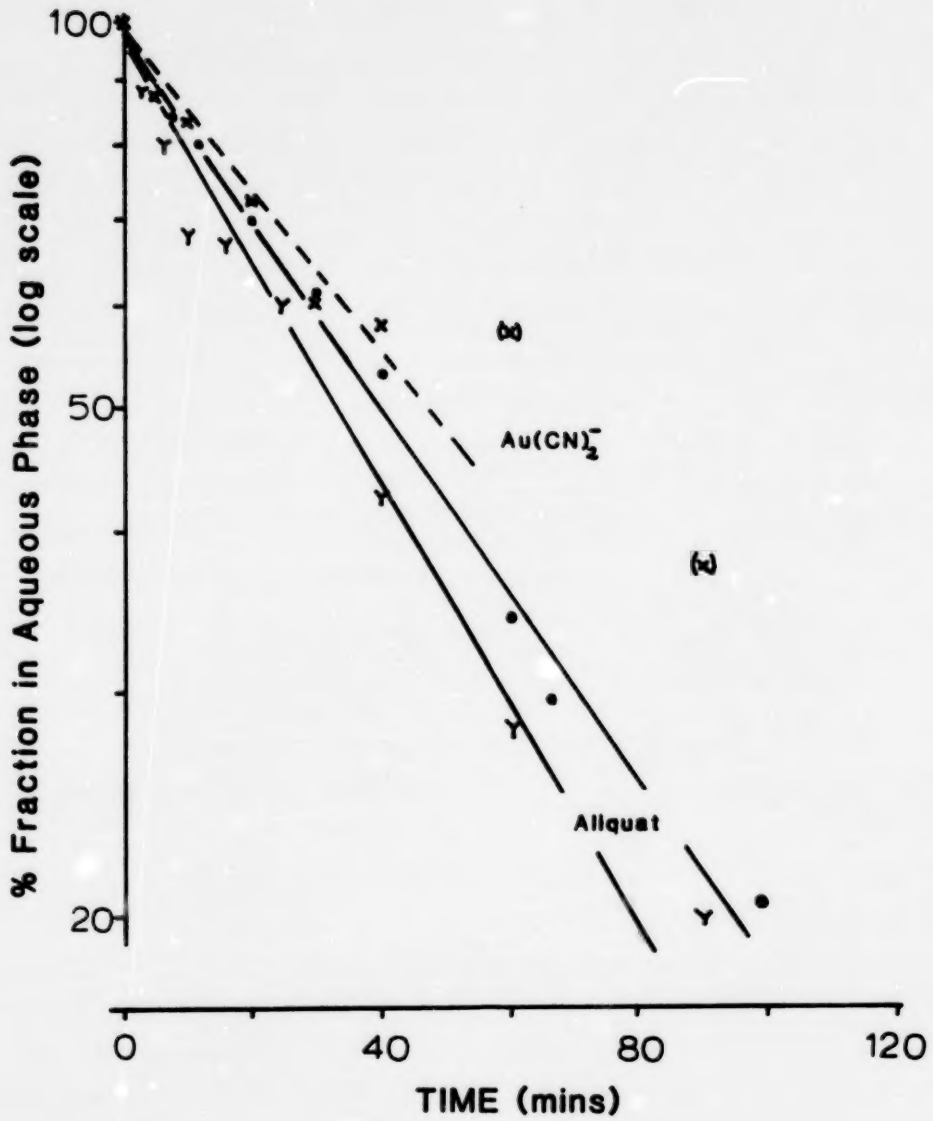
Conditions: Aqueous (300 mls) 200 ppm NaCN
Organic (150 mls) 5% Aliquat 336 in Solvesso 150
Stirring speed magnet ~ 120 ppm
Interfacial area = 75 cm^2
Initial $[Au(CN)^-_2]$ = 7.0 ppm.
Final [Aliquat] = 450 ppm or 35 ppm.

the water phase remains the same indicative of first order kinetics. Significantly, the rate of $Au(CN)^-_2$ extraction is about the same as the rate of Aliquat transfer suggesting that in both cases the rate determining factor is the transfer across the interface. In these tests with rather poor hydrodynamic control the initial of $Au(CN)^-_2$ extraction into 5% Aliquat 336 is about 7.10^{-7} M per hour per cm^2 interfacial area (Fig. 20) which is about 5 times slower than that reported by Fuerstenau et al for $CuCl^{2-}_4$ [71] under optimum stirring conditions. However, more definitive tests with a proper cell would be required to properly establish gold extraction kinetics.

When the data in Figure 20 was plotted on a log scale, good straight lines were obtained over the first hour (Fig. 21) typical of first order kinetics. Slightly slower rates of $Au(CN)^-_2$ extraction after 1 hour may be due to interfacial ion-pairing becoming rate determining.

The main conclusion from this work is that both the rate of gold extraction and Aliquat transfer are interfacially controlled with little significant difference in rates. Thus transfer of Aliquat to the pulp, via the aqueous phase, is inevitable before all the $Au(CN)^-_2$ can be extracted and this will lead to gold adsorption onto the pulp.

In a Graesser contactor system or column system with a static organic layer, extraction times of several hours would be necessary to recover >95% $Au(CN)^-_2$ because of the low interfacial surface area. The poor gold extraction reported by Gao and Molnar [45] from the initial operation of the Graesser Mixer with SIP can be attributed, in part, to poor mixing characteristics of the pulp and aqueous phases, and, in part, to gold adsorption on the pulp itself, following Aliquat adsorption. It is predicted that improved mixing of the pulp will lead to increased Aliquat loading and further gold losses. Addition of HDNNS as suggested by Abotsi and Osseo-Asare may result in less $Au(CN)^-_2$ adsorption by itself, but is likely to cause increased Aliquat adsorption and hence exacerbate the gold loss problem.



Fic 21 - First-order kinetic plots of rates of Aliquat 336 and $Au(CN)^-_2$ transfer between water and kerosene phases.

Conditions: Aqueous (300 mls) 200 ppm NaCN
Organic (150 mls) 5% Aliquat 336 in Solvesso 150
Stirring speed magnet 120 ppm
Interfacial area 75 cm^2
Initial $[Au(CN)^-_2]$ = 7.0 ppm.
Final [Aliquat] = 450 ppm or 35 ppm

Overall Conclusions and Recommendations

The successful operation of a solvent-in-pulp process requires an optimal balance of chemical, physical, kinetic, equilibrium and engineering factors, all taxing the skills of the hydrometallurgist, mineralogist, mineral processor, and surface chemist. There are many pitfalls for the unwary and traps for the uninitiated.

This review and investigation has shown that optimization of the chemistry does not necessarily point the way to the future. The best extractant system for $Au(CN)^-_2$, mainly a quaternary amine, also appears to be one of the most active surfactant systems due to its cationic charge interacting with predominantly negatively charged mineral surfaces in alkaline cyanide solutions. No effective way of inhibiting or desorbing the quaternary amine, and no way of preventing its transfer to the mineral has yet been identified.

Although reasonable organic losses can be tolerated the most serious aspect of quaternary amine absorption onto minerals appears to be its affinity for $Au(CN)^-_2$ thus making the ore slurry "carbonaceous and refractory". Any addition agents designed to inhibit cationic quaternary amine adsorption seem likely to enhance anionic $Au(CN)^-_2$ adsorption and vice-versa. Thus there seems to be an unresolvable dichotomy. There is a similar problem in designing a contactor which can extract $Au(CN)^-_2$ at reasonable rates yet prevent solids from mixing with the organic phase and forming cruds or emulsions.

Most of the problems with SIP come from the need to control fines or from the high surface area of mineral. It is therefore recommended that SIP be applied first to coarsely ground ores, provided that the metal value can be sufficiently well-liberated. With fine ores it is recommended that either neutral or anionic extractants, with minimum alkyl chain length consistent with reasonably low water solubility, be examined for their adsorption onto silicate and pyrite ores. It is also necessary to examine

their effect on adsorption of metal values from solution onto the slurry.

In view of the slow extraction kinetics inherent with the Graesser Contactor, it is also recommended that further consideration be given to the design, with the object of separating the underflow from the clarified supernatant. Vigorous stirring of the clarified supernatant with the organic would allow gold to be extracted quickly whilst the underflow is washed in stages to prevent contact with quaternary amine.

The quaternary amine extractant system, coupled with the novel air-sparged thiourea stripping procedure developed at CANMET, appears to have merits for clarified leach solutions, and exhibits low water-soluble solvent losses. It is recommended that sources of high grade gold leach liquors be investigated for further development tests and an economic analysis be carried out to determine lowest viable $Au(CN)^-_2$ concentration for possible application to heap leach liquors.

Whilst SIP appears to offer the best cost savings and to be competitive with RIP if solvent losses to the solids and to raffinate can be controlled to modest levels, an economic analysis of the cost of gold processing shows that there is limited scope to improve on overall CIP technology costs because this represents only a small fraction of the overall cost of gold operation. It is recommended that labour costs associated with gold recovery from leach liquors be examined to try to identify significant cost savings through simplification of unit operations and minimising of man-power.

Acknowledgements

The author would particularly like to thank Mr. G.M. Ritcey, Dr. P. Riveros and Ms. E.W. Wong for several useful discussions and background information, and also Dr. R. Molnar and Ms. Andrea Bernolak and Jill Sunstrum for their helpful contributions. The gold A.A.S. analyses were carried out by Mr. B. Taylor and his sufferance in sharing his laboratory is appreciated. The Industrial Minerals Section of CANMET is thanked for their instruction and guidance in determining surface areas.

This study was made possible by the granting of Study Leave by Murdoch University.

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